U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-256 020

Fuel Contaminants
Volume 1
Chemistry

Battelle Columbus Labs.

Prepared For:
Industrial Environmental Research Lab.

July 1976

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/2-76-177a	2.	3. RECIPIENT'S ACCESSION NO.
4. TITLE AND SUBTITLE Fuel Contaminants: Volume 1. Chemistry		5. REPORT DATE July 1976 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) E. J. Mezey, Surjit Singh, and D. W. Hissong		8. PERFORMING ORGANIZATION REPORT NO
9. PERFORMING ORGANIZATION NAME AND ADDRESS Battelle-Columbus Laboratories 505 King Avenue Columbus, Ohio 43201		10. PROGRAM ELEMENT NO. EHB529 11. CONTRACT/GRANT NO. 68-02-2112
12. SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Research and Development Industrial Environmental Research Laboratory Research Triangle Park, NC 27711		13. TYPE OF REPORT AND PERIOD COVERED Task Final; 6/75-2/76 14. SPONSORING AGENCY CODE EPA-ORD

15. SUPPLEMENTARY NOTES Project officer for this report is W. J. Rhodes, mail drop 61, 919/549-8411, ext 2851.

16. ABSTRACT The report reviews information on the characteristics of solid and liquid fuels. Specifically, it deals with the chemical and physical characteristics of components of the fuel which are sources of sulfur, nitrogen, and trace element pollutants when that fuel is utilized. The review suggests that at least part of the sulfur and most of the nitrogen originate from compounds common to the fuels reviewed (coal, petroleum, tar sand oil, and shale oil). These are primarily organic sulfur and organic nitrogen compounds. For liquid fuels, it was concluded that intrinsic centers of sulfur and nitrogen contamination are found in the colloidal suspensions commonly known as asphaltenes and the more soluble resins. Trace elements are present as oil-soluble compounds in petroleum, tar sand oil, and shale oil. In coal, it was concluded that the nitrogen contaminants are present as organic compounds and that the sulfur is present both as organic and inorganic compounds. Trace elements in coal were categorized into those found principally with the organic matter of coal and those found present principally in the mineral matter associated with coal.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Pollution	Sulfur	Pollution Control	13B	07B
Fuels	Nitrogen	Stationary Sources	21D	
Contaminants	Trace Elements	Solid Fuels		06A, 06P
Chemistry		Liquid Fuels	07	
Chemical Properties			07D	
Physical Properties				

18. DISTRIBUTION STATEMENT Unlimited	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES 177
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE 7.50

EPA Form 2220-1 (9-73)

PRICES SUBJECT TO CHANGE

229185

PB 256 020

EPA-600/2-76-177a
July 1976

Environmental Protection Technology Series

FUEL CONTAMINANTS:
Volume 1. Chemistry

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

[illegible]
[illegible]
[illegible]
[illegible]

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Development, U.S. Environmental Protection Agency, have been grouped into five series. These five broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The five series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies

This report has been assigned to the ENVIRONMENTAL PROTECTION TECHNOLOGY series. This series describes research performed to develop and demonstrate instrumentation, equipment, and methodology to repair or prevent environmental degradation from point and non-point sources of pollution. This work provides the new or improved technology required for the control and treatment of pollution sources to meet environmental quality standards.

EPA REVIEW NOTICE

This report has been reviewed by the U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policy of the Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161.

EPA-600/2-76-177a
July 1976

FUEL
CONTAMINANTS
VOLUME 1. CHEMISTRY

by

E. J. Mezey, Surjit Singh, and D. W. Hissong

Battelle-Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

Contract No. 68-02-2112
Program Element No. EHB529

EPA Project Officer: William J. Rhodes

Industrial Environmental Research Laboratory
Office of Energy, Minerals, and Industry
Research Triangle Park, NC 27711

Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development
Washington, DC 20460

ABSTRACT

Volume I of this two-volume report reviews information on the characteristics of solid and liquid fuels. Specifically, this volume deals with the chemical and physical characteristics of components of the fuel which are sources of sulfur, nitrogen, and trace element pollutants when these fuels are utilized.

This review suggests that at least part of the sulfur and most of the nitrogen originate from compounds common to the fuels reviewed, i.e., coal, petroleum, tar sand oil, and shale oil. These are primarily organic sulfur and organic nitrogen compounds. For liquid fuels, it was concluded that intrinsic centers of sulfur and nitrogen contamination are found in the colloidal suspensions commonly known as asphaltenes and the more soluble resins. Trace elements are present as oil soluble compounds in petroleum, tar sand oil, and shale oil. In coal, it was concluded that the nitrogen contaminants are present as organic compounds and that the sulfur in coal is present both as organic and inorganic compounds. The organic sulfur and nitrogen contaminants are part of the three-dimensional carbon skeletal structure that makes up the organic part of coal. The major sources of inorganic sulfur are pyrites and sulfates. Trace elements in coal were categorized into those found principally with the organic matter of coal and those found present principally in the mineral matter associated with coal. Upon conversion of coal to a coal liquid, most of the organic sulfur and nitrogen originally present in the coal remain in the coal liquid. Most of the trace elements associated with the mineral matter remain insoluble. Such characterizations were done in part to facilitate the review of methods of removal of contaminants prior to combustion of the fuel reported in Volume II.

TABLE OF CONTENTS

Page

ABSTRACT iii

1. INTRODUCTION 1

    1.1. Technical Objectives. 1
    1.2. Approach. 1
    1.3. Background. 2

        1.3.1. Characteristics of Coal. 6
        1.3.2. Characteristics of Petroleum or Crude Oils . 14
        1.3.3. Characteristics of Tar Sands 15
        1.3.4. Characteristics of Shale Oil 17

2. CHARACTERIZATION OF CONTAMINANTS IN FUELS. 25

    2.1. Sulfur Contaminants in Fuels. 25

        2.1.1. Sulfur Contaminants in Coal/Coal Liquids . . 25
        2.1.2. Sulfur Contaminants in Petroleum or Crude Oils 31
        2.1.3. Sulfur Contaminants in Tar Sand Oil. 34
        2.1.4. Sulfur Contaminants in Shale Oil 35

    2.2. Chemical and Physical Characteristics of Organic Sulfur Contaminants in Fuels. 35

        2.2.1. Mercaptans (Thiols). 38
        2.2.2. Sulfides 41
        2.2.3. Disulfides 44
        2.2.4. Heterocyclic (Thiophene) 47

    2.3. Nitrogen Contaminants in Fuels. 52

        2.3.1. Nitrogen Contaminants in Coal/Coal Liquids . 52
        2.3.2. Nitrogen Contaminants in Petroleum 56
        2.3.3. Nitrogen Contaminants in (U.S.) Tar Sand/Oil 60
        2.3.4. Nitrogen Contaminants in Shale Oil 60

    2.4. Chemical and Physical Characteristics of Organic Nitrogen Contaminants in Fuels. 64

        2.4.1. Pyrroles 66
        2.4.2. Indole 67
        2.4.3. Carbazoles 67
        2.4.4. Benzonitriles. 68

TABLE OF CONTENTS (Continued)

Page

2.4.5. Benzamide 68
2.4.6. Phenazine 68
2.4.7. Acridine. 69
2.4.8. Amines 69

2.5. Characteristics of Trace-Element Contaminants in Coal/Coal Liquids 72

2.5.1. Trace Elements Identified in Coal. 75
2.5.2. Trace Elements Associated With Mineral Matter in Coal 83
2.5.3. Trace Elements Associated With Organic Matter in Coal 92
2.5.4. Characteristics of Nonmetallic Trace Elements in Coal 98

2.6. Characteristics of Trace Elements in Liquid Fuels (i.e., Petroleum, Tar Sand Oils, and Shale Oils). . . 106

2.6.1. Trace Elements Identified in the Liquid Fuels. 107
2.6.2. Trace Elements Associated with Petroleum Mineral Matter 115
2.6.3. Trace Elements Associated with Petroleum Organic Matter 117
2.6.4. Trace Elements in Tar Sand Oils and Shale Oils 139

3. CONCLUSIONS 144

3.1. Contaminants in Solid Fuels 144

3.2. Contaminants in Liquid Fuels 146

3.3. Distribution of Contaminants in Fuels. 148

3.3.1. Sulfur and Nitrogen Contaminants 148
3.3.2. Trace Elements 150

3.4 Potential for Removal of Contaminants. 153

3.4.1. Contaminants Present as Discrete Phases 153
3.4.2. Contaminants Present as Part of Fuel Structure 155

4. REFERENCES

4.1. Fuel and Fuel Contaminant Characterization. 156

LIST OF TABLES

Page

Table 1. Search Terms and Strategy. 3

Table 2. Results of Electronic Data Base Literature Search. . . 4

Table 3. Classification of Coal by Rank 10

Table 4. Analysis of Some Representative Crude Oils 14

Table 5. Elemental Analysis of Some Tar Sands 16

Table 6. Chemical Analysis and Molecular Weights of Tar Sands Bitumen, Coal Liquids, and Their Fractions 18

Table 7. Composition of Colorado Shale Oil. 19

Table 8. Mineral Matter of Oil Shales 21

Table 9. Percentage of Colorado Oil Shale as Minor Elements . . 22

Table 10. Typical Ultimate Analysis of Oil-Shale Kerogen 22

Table 11. Some Organic Sulfur Compounds Present in Coal Products. 27

Table 12. Estimates of the Sulfur Content in Eastern and Western Coal Reserves. 30

.able 13. Sulfur Present as Constituents Indicated in Crude Oils 32

Table 14. Sulfur Compounds in Tar Sand Oils. 34

Table 15. Average Distribution of Sulfur in Colorado Mineable-Bed Oil Shales. 36

Table 16. Sulfur-Type Compounds in Colorado Shale Oil Naphtha. . 36

Table 17. Boiling Point, Density, and Solubility in Water of Various Mercaptans. 39

Table 18. Boiling Point and Density of Alkyl Sulfides. 42

Table 19. Boiling Point and Density of Various Disulfides. . . . 45

Table 20. Boiling Point, Density, and Freezing Point of Thiophene and Some Derivatives 48

Table 21. Nitrogen Content of U.S. Coals 53

Table 22. Bituminous Coal Treatment and Determination of Nitrogen Bond Types. 54

Table 23. Nitrogen Compounds and Building Blocks in Tars 54

Table 24. Nitrogen Compounds in Creosote Oil and Coal Tar Pitch. 57

Table 25. Distribution of Nitrogen in Crude Oil. 59

Table 26. Nitrogen Compounds in Petroleum. 59

LIST OF TABLES (Continued)

Table 27. P.R. SPRINGS, UTAH, BITUMENS 61

Table 28. Gross Composition of Selected Bitumen. 61

Table 29. Nonhydrocarbon Concentrate P.R. SPRINGS BITUMEN. . . . 62

Table 30. Nitrogen Distribution in Shale-Oil Fractions 63

Table 31. Nitrogen Compounds in Shale Oil. 63

Table 32. Nitrogen Type Analysis of Shale Oil Distillate 65

Table 33. Physical Properties of Some Amines Found in Fuels. . . 70

Table 34. Precision on NBS-EPA Round-Robin Coal Sample 77

Table 35. Elemental Composition of NBS-EPA Coal and Fly Ash Standards. 78

Table 36. Mean Analytical Values for 101 Coals 80

Table 37. Distribution of Trace Elements in Coal Seams and Probable Mode of Mineralization. 82

Table 38. Correlation of Trace Element Distribution in Washed Coal Fractions. 84

Table 39. Average Organic Affinity of Some Metals Determined by Float-Sink Methods 85

Table 40. Affinity of Elements for Pure Coal and Mineral Matter as Determined from Float-Sink Data. 86

Table 41. Minerals Associated with British Bituminous Coals. . . 90

Table 42. Trace Element--Coal Mineral Species Correlations . . . 91

Table 43. Forms of Binding of Germanium in Solid Fuels 95

Table 44. Ratio of Na + K to Cl in Coal and Solubilized Chloride Salts 102

Table 45. Ratios of Cl, Br, and I Found in Coal. 105

Table 46. Distribution of 28 Trace Metals in Ashes of 24 Crude Oils. 108

Table 47. Summary of the Analysis of Oil-Soluble Ash in 25 Crude Oils. 109

Table 48. Trace-Element Contents of Four Crude Oils Obtained by Neutron-Activation Analysis. 111

Table 49. Detection Limits for Different Elements in a "Typical" Crude Oil Matrix in PPB. 112

Table 50. Typical Salt Contents of Crude Oils. 116

LIST OF TABLES (Continued)

Page

Table 51. Distribution of Percentage of Total Nitrogen of Crude in Resins and Asphaltenes. 126

Table 52. Distribution of Trace Elements in Components of a California Crude Oil. 128

Table 53. Distribution of Molecular-Weight Fractions of Oil Compounds 130

Table 54. Distribution of Trace Elements in Asphaltenes 131

Table 55. Distribution of Trace Elements in Resins. 132

Table 56. Distribution of Trace Elements in Methanol-Soluble Fractions 133

Table 57. Distribution of Nickel and Nickel Porphyrin in Asphaltenes and Resins from a California Tertiary Oil. 135

Table 58. Resins and Asphaltene Content of Tar Sand Oils, Shale Oil Fractions, and Coal Liquids 140

Table 59. Porphyrin and Trace-Metal Contents of Certain Asphaltic Oils. 142

Table 60. Elemental Analysis of Typical Fuels 145

Table 61. Distribution of S and N Contaminants in Fuels 149

Table 62. Trace Elements Associated with Mineral Matter in Solid and Liquid Fuels. 151

Table 63. Trace Elements Associated with Organic Matter of Solid and Liquid Fuels. 152

Table 64. Metal Contaminants Associated with Organic Matter in Coal and Compared to their Presence in Petroleum . . 154

LIST OF FIGURES

Page

Figure 1. Tomkeieff's Classification of Carbonaceous substances 5

Figure 2. Coal Structures with Probable Sulfur and Nitrogen Compounds 12

Figure 3. Building Blocks of Coal (Wender). 13

Figure 4. Arrangement of Tar Sand Particles and Bitumen. 16

Figure 5. Generalized Structure of Kerogen from Colorado and Products from Thermal Fragmentation of Kerogen 23

Figure 6. Nitrogen Compounds Extracted from Coal Precursors, e.g., Humic Acids, Peat 55

Figure 7. Representative Basic and Nonbasic Nitrogen Compounds in Petroleum Products. 58

Figure 8. Occurrence Frequency of Elements in 13 Raw Coals as Determined by Spark-Source Mass Spectrometry 76

Figure 9. Concentration Range of Elements in 13 Raw Coals Analyzed by Spark-Source Mass Spectrometry 76

Figure 10. Relation of Organic Affinity and Ionic Potential of the Elements. 97

Figure 11. Trace Elements Identified in Petroleum and Shale Oils.

Figure 12. The Porphin Structure and Well Known Porphyrins Containing the Structure 120

Figure 13. Tetradentate Metal Complexes of Nickel and Vanadium with Mixed Ligand Atoms 122

Figure 14. Model Defect Site (or Gaps) in an Aromatic Sheet of the Asphaltene Structure 122

Figure 15. Effect of Asphaltenes Content on Sulfur and Metals in Six Fractions of Ultracentrifuged Oil 124

1. INTRODUCTION

1.1. Technical Objectives

The overall objective of this study is to identify by means of a literature survey possible future environmental control techniques for potential pollutants in solid and liquid fuels which use as their approach the removal of such contaminants from the fuels before combustion. The program included a survey and subsequent evaluation of techniques both past and present plus evaluation of potential new and unique techniques based on detailed basic studies of the fuel-contaminant chemistry and potential removal mechanisms that may be applicable to fuels. Primary emphasis is on the removal of sulfur and nitrogen, but removal of other contaminants such as trace elements and their compounds which are potential pollutants of interest or concern are also considered. These include, but are not linked to, the following which are listed in a tentative order of priority: Hg, Be, Cd, As, Pb, Cu, V, Ni, Se, Mn, Sn, F, Cl, Ga, Co, Cr, Ge, Te, B, Br, Mo, Zn, Zr, and P.

1.2. Approach

The approach used to fulfill these objectives was to identify the chemical and physical nature of general groups of contaminants and specific contaminants through a literature survey. In addition, the problems of removing such contaminants from fuels were discussed. The literature survey was to identify contaminant-removal methods which have been successfully used in the past and/or are currently being utilized and also to look at techniques which were previously unsuccessful but in today's world might be. These removal methods were systematically categorized according to the mechanism for removal and the contaminant(s) removed. The nature of the removal process, what it achieved, and how it achieved the removal were analyzed and are discussed in a separate volume.

An electronic search of the literature was made by the EPA Library at Research Triangle Park and the Battelle Energy Information Center using the search terms and strategy given in Table 1. The output from these searches produced over 8,000 citations from the data bases given in Table 2, which were then hand sorted and placed into a keysort information storage, and retrieval system. Additional search of the literature to identify older contaminant removal methods was done by hand using Chemical Abstracts. To cover the intervening periods, extensive use of the review articles and books was made.

This report is divided into two volumes. The first volume covers the identification and characterization of sulfur, nitrogen, and trace-element contaminants in coal, coal liquids, petroleum, tar sand oils, and shale oils. The second volume lists and discusses methods for contaminant removal under five or six broad categories of methods used for these fuels.

1.3. Background

In order to better understand the characteristics of the sulfur, nitrogen, and trace-element contaminants in solid and liquid fuels, a brief review of these fuels seems appropriate.

The carbonaceous fuels that will be discussed here were classified by Tomkeieff(1)* as shown in Figure 1. In this figure the fuels are further subdivided into liptobiolites, coals, and bitumens. The liptobiolites consist primarily of resins, waxes, and spores and represent the more stable residues of decomposed land plants. The coals are subdivided into the humic series, the humic-sapropelic series, and the sapropelic series. The humic coals are the common coals (lignite to anthracite) formed from peat swamp type deposits. The sapropelic coals were formed in stagnant water from the remains of aquatic organisms that were primarily plantonic. The humic-sapropelic type coal was formed by a combination of the conditions that produced the humic and sapropelic coals. The bitumens are naturally occurring hydrocarbons (including petroleum, asphalt-like material, and

---

* References are cited at the end of this report.

TABLE 1. SEARCH TERMS AND STRATEGY

Fuel

Coal (Bituminous Coal) (Lignite) (Subbituminous Coal)
Oil (Crude) (Crude Oil) (Petroleum) (Oils) (Crude Oils)
Shale Oil (Oil Shale) (Kerogen)
Tar Sands
Coal Liquids

Processes

I	Cleaning	Coal
	Washing	
	Leaching	
	Chemical Treatment	
	Hydrogenation	
	Desulfurization	
	Hydrodesulfurization	
	Sulfur Removal (not stack or flue gas)	
	Preparation	
	Beneficiation	
	Liquefaction	
	Deashing	
II	Desalting	Oils
	Washing	
	Deasphalting	
	Asphaltene Removal	
	Demetallization	
	Metal Removal	
	Denitrification	
	Nitrogen Removal	
	Hydrodesulfurization	
	Deashing	

Contaminants

Sulfur	Coal, Oils
Nitrogen	
Mineral(s)	
Asphaltene	
Halides	
Halogens	
Contaminant	
Contamination	
Trace Element(s)	
Trace Metal(s)	
Metal(s) et al	
Nickel	
Mercury	
Cadmium	
Arsenic	
Lead	
Copper	
Vanadium	
Selenium	
Manganese	
Tin	
Fluorine	
Chlorine	
Gallium	
Cobalt	
Chromium	
Germanium	
Boron	
Molybdenum	
Zinc	
Zirconium	
Phosphorus	
Berylium	
Tellurium	
Bromine	

Search Procedure

Combine Fuels and Equivalents
Separate
Coal
Oils
Coal Liquids

Combine Processes
Separate
I
II

Combine Contaminants

Search Strategy

Coal and I but not Flue/Stack Gas
Coal and Contaminants but not Flue/Stack Gas
Coal Liquids and II
Coal Liquids and Contaminants
Oils and II
Oils and Contaminants

Suggested Data Bases to be Searched

Chem Abs
NTIS
Engineering Index
ERDA-Recon
Energy Research and Development
Coal Data Base
NSA(?)
APIC
Physics Index Abstracts
Geological Reference File
Pollution Abstracts

TABLE 2. RESULTS OF ELECTRONIC DATA BASE LITERATURE SEARCH

Data Base	Coverage Subject	Coverage Years	Citations Printed[a]
Battelle Energy Information Center (Basis 70)	Coal, Petroleum Shale Oil, Tar Sands	1932-present	576
American Petroleum Institute	Petroleum	1972-1975	941
Smithsonian Science Information Exchange	Coal Cleaning Research	?	76
(Currently Funded Projects)	Fossil Fuels (Minus Coal)	?	170
Geological Reference File	Coal	1967-present	476
	Petroleum	1964-present	229
National Technical Information Service	Coal	1964-present	382
	Petroleum	1964-present	104
Engineering Index	Petroleum	1969-present	694
	Coal	1970-present	186
Chemical Abstracts Service (Chem 70-71)	Coal	1970-present	1511
	Petroleum Contaminants	1970-1971	449
	Pet. Contam. Removal	1970-1971	335
(CHEMCON)	Petroleum Contaminants	1972-present	625
	Pet. Contam. Removal	1972-present	1548
	Total Citations		8302

(a) The number of citations are for as-received outputs with no screening of relevant articles or titles.

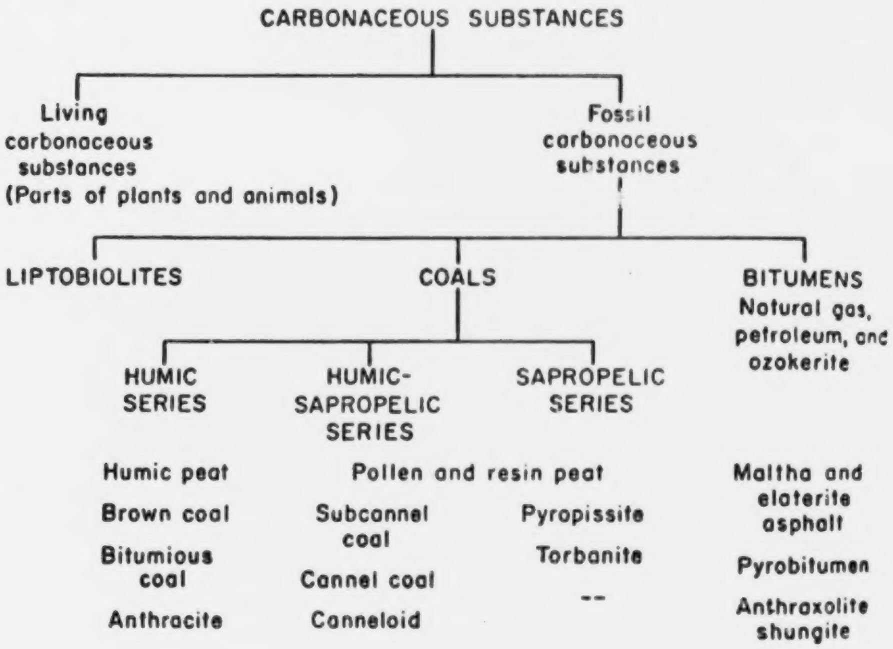

CARBONACEOUS SUBSTANCES
Living carbonaceous substances (Parts of plants and animals)
Fossil carbonaceous substances
LIPTOBIOLITES
COALS
BITUMENS
Natural gas, petroleum, and ozokerite
HUMIC SERIES
HUMIC-SAPROPELIC SERIES
SAPROPELIC SERIES
Humic peat
Brown coal
Bitumious coal
Anthracite
Pollen and resin peat
Subcannel coal
Cannel coal
Canneloid
Pyropissite
Torbanite
--
Maltha and elaterite asphalt
Pyrobitumen
Anthraxolite shungite

FIGURE 1. TOMKEIEFF'S CLASSIFICATION OF CARBONACEOUS SUBSTANCES(1)

oil shale) and are soluble in carbon disulfide. The coals of the humic series are discussed in the next section. Cannel coal, which has a dark grey color, is a rare coal that occurs in nonbanded massive structures and usually breaks with a concoidal fracture. Cannel coal burns readily with a bright flame. The canneloid coal is like cannel coal in some respects but contains less volatile matter. Pyropissite and torbanite are two kinds of sapropelic coals. Pyropissite is like lignite (brown coal) and is a source for montan wax. Torbanite coal was formed from algal mass. Among the bitumens, ozokerite is a hard, waxy, jet black hydrocarbon that is soluble in turpentine and chloroform. Ozokerite is finely disseminated in the rock unlike gilsonite which occurs as veins. Maltha and elatenite are viscous tar-like materials. The Pyrobitumen and anthroxolite are types of heavy (tar-like) bitumen.

Summaries of the physical and chemical characteristics of coal, coal liquids, petroleum, tar sand oil, and shale oil are given in the following sections.

1.3.1. Characteristics of Coal

Physical Characteristics. Coal has been defined appropriately as an organic rock and as such it is not a homogeneous substance in either chemical composition or physical appearance. Most coals with ranks from lignites to anthracites appear to consist of alternating bands of bright and dull material. These bands vary in width from a few millimeters to several centimeters. In some coals, the bright layers comprise by far the larger part, while in others they make up only a small portion of the cross section or are entirely absent. In banded bituminous coal, the bands are discontinuous and appear to be embedded in a continuous mass. These bands of heterogeneity in the physical aggregation of coal provide paths and channels into coal for diffusion of appropriate desulfurizing and denitrification reagents.

The bands differ greatly in color, texture, and luster. The bright bands are homogeneous, compact, jet black, and often glossy in appearance. The duller material is grayish and more granular in appearance, and the surface is irregular and rough. The macroscopic components found in coal are commonly referred to as lithotypes (rock types). These lithotypes are further described in the "European System" as:

(1) Vitrain, a uniform bright material, referred to as anthraxylon in the U.S. Bureau of Mines classification of coal.

(2) Clarain, which has a surface luster that is inherently banded. It contains considerable amounts of translucent material, as well as large proportions of voids, resin, and opaque material.

(3) Durain, which has a hard, granular appearance. It is practically structureless and dull black in color. There is no equivalent of clarain and durain in the Bureau of Mines classification system but the term attritus describes the dull bands that consist of plant debris.

(4) Fusain, which occurs as patches, consists of powdery, readily detachable, fibrous strands and is often referred to as "mineral charcoal". The term is also used in the Bureau of Mines classification.

The lithotypes are further subdivided into homogeneous microscopic constituents which are called macerals. The most common macerals specially relevant to U.S. coals are:

(1) Vitrinite, the principal coal maceral and the primary constituent of bright coal. This is readily soluble in a range of organic solvents, including polycyclic aromatics (anthracene oil).

(2) Fusinite, the maceral found in fossil charcoal. This does not swell, soften, or cake on heating, and particles of fusinite can still be recognized as such under the microscope after pyrolysis.

(3) Sporinite, the fossil remains of spores. This becomes extremely fluid on heating to 400-450 C, and at these temperatures yields large amounts of the volatile matter.

(4) Micrinite, the maceral, which is completely structureless. This was probably derived from humic mud. It is a majur ingredient of dull coal. Like fusinite, this maceral is inert.

These macerals can be removed from coal by techniques developed by Kroger, Van Krevelen, and others (2) (the order of densities among macerals from any one coal is fusinite > micrinite > vitrinite > sporinite). By similar separation of appropriate lithotypes, high concentrates of micrinites and fusinites can also be obtained from some coals.

Pores and Capillaries of Coal. The presence of naturally occurring pores, capillaries, and channels in coal plays a prominent role in making the internal part of coal accessible to solvents and gaseous reagents. The rank of coal is basically an indication of the carbon content and is also a good indicator of the pores in coal. High-rank coal approaches a graphite lattice structure. Some of the openings in bituminous coals are ultrafine, just a few angstroms wide, while others are as large as 100 A. In addition, there are cracks which are larger and contribute from 20 to 50 percent of the total internal free volume. (2) The surface area can be measured by heat of wetting of methanol or by adsorption of inert gases. Discrepancies in the surface area observed at low temperatures (liquid nitrogen) have been attributed to the decrease in molecular diffusion and collapse of capillaries at low temperatures. Walker (3) has shown that for American coals the surface area as measured at 77 K and 298 K using nitrogen and carbon dioxide, respectively, indicate fine microporosity in the 4 to 5 A range. Both the low-rank coals (<70 percent carbon) and high-rank coals (90 percent carbon) have a large surface area (300 to 400 m^2/g), whereas for coals of intermediate rank (78 percent carbon), the amount of surface area is at a minimum. Large voids of up to 30,000 A are present in most coals. Smaller voids of 12 to 300 A are called transitional pores. There exists no clear relationship between total surface area and coal rank, but lower tank coals generally have a larger percentage of their total surface area due to larger pores.

The value measured for the surface area of coal depends largely on the reagent and temperature used in the determination. While processing coal to remove contaminants, the temperature or the reagent selected could be crucial in utilizing the inherent surface area of coal. Bituminous coals are known to become plastic or fluid-like between 400 to 430 C, so that at this temperature the surface areas would be at a minimum. As most coals are heated to higher temperatures, there occur physical and chemical changes leading to increases in surface area. The treatment of coal with reactive reagents, e.g., benzene or pyridine, begins to dissolve the coal particle starting from the surface of contact. In such a case, the fine capillaries in the structure would serve no purpose, but the large voids could promote faster penetration. In the case of high temperatures (400 to 450 C) and with coal-derived solvents (anthracene oil, a polynuclear aromatic mixture), the surface area loses all significance as a pathway for diffusion processes as at this temperature coal is solubilized.

Types of Coal. In the standard ASTM classification of coal, coal is ranked according to fixed-carbon content, volatile matter content, and heating value. There is no sharp line of demarcation between the properties of coals of different ranks, but each merges gradually into those of the adjacent group. The coal classification by rank is shown in Table 3. Wide variations may be encountered in the analysis, not only for each rank of coal, but also for those from each seam and from each individual mine.

The bituminous and subbituminous coals are also classified, in the U.S. System, as to type according to the relative amounts of the petrographic constituents, anthraxylon, and the finely divided attritus matter, both translucent and opaque. The banded coals are divided into three types: (1) bright coals, (2) semisplint coal, and (3) splint coal. The bright coals consist principally of anthraxylon and attritus, with the translucent type predominating. The semisplint coals are also made up of anthraxylon and attritus but in about the same relative proportions. Most of the U.S. coals are bright coals. The splint and semisplint coals seldom occur by themselves, but are usually associated with bright coals in the bed. The splint coals are harder than bright coals, and more solid and less friable than the bright and semisplint coals.

TABLE 3. CLASSIFICATION OF COAL BY RANK(a)

Class	Group	Fixed carbon limits, % (dry m.m.f. basis)		Volatile matter limits, % (dry m.m.f. basis)		Calorific value limits, B.t.u./lb. (moist[b] m.m.f. basis)		Agglomerating character
		Equal or greater than	Less than	Greater than	Equal or less than	Equal or greater than	Less than	
Anthracitic	Meta-anthracite	98	. . .	. . .	2	. . .	. . .	Non-agglomerating
	Anthracite	92	98	2	8	. . .	. . .	
	Semianthracite[c]	86	92	8	14	. . .	. . .	
Bituminous	Low-volatile bituminous coal	78	86	14	22	. . .	. . .	Commonly agglomerating[e]
	Medium-volatile bituminous coal	69	78	22	31	. . .	. . .	
	High-volatile *A* bituminous coal	. . .	69	31	. . .	14,000[d]	. . .	
	High-volatile *B* bituminous coal	. . .	. . .	. . .	. . .	13,000[d]	14,000	
	High-volatile *C* bituminous coal	. . .	. . .	. . .	. . .	11,500	13,000	
						10,500	11,500	Agglomerating
Subbituminous	Subbituminous *A* coal	. . .	. . .	. . .	. . .	10,500	11,500	Non-agglomerating
	Subbituminous *B* coal	. . .	. . .	. . .	. . .	9,500	10,500	
	Subbituminous *C* coal	. . .	. . .	. . .	. . .	8,300	9,500	
Lignitic	Lignite *A*	. . .	. . .	. . .	. . .	6,300	8,300	
	Lignite *B*	. . .	. . .	. . .	. . .	. . .	6,300	

[a] A.S.T.M. Designation D 388-36. Data from U.S. Bureau of Mines. This classification does not include a few coals, principally non-banded varieties, which have unusual physical and chemical properties and which come within the limits of fixed carbon or calorific value of the high-volatile bituminous and subbituminous ranks. All these coals either contain less than 48% dry m.m.f. fixed carbon or have more than 15,500 moist m.m.f. B.t.u./lb.

[b] Moist refers to coal containing its natural inherent moisture but not including visible water on the surface of the coal.

[c] If agglomerating, classify in low-volatile group of the bituminous class.

[d] Coals having 69% or more fixed carbon on the dry m.m.f. basis are classified according to fixed carbon, regardless of calorific value.

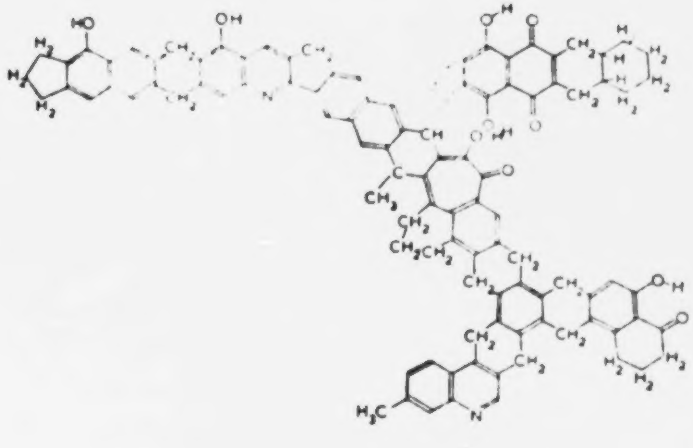
[e] There may be non-agglomerating varieties in these groups of the bituminous class, and there are notable exceptions in the high-volatile C bituminous group.

(a) Source: Chem. Eng. Handbook, Perry (1973).

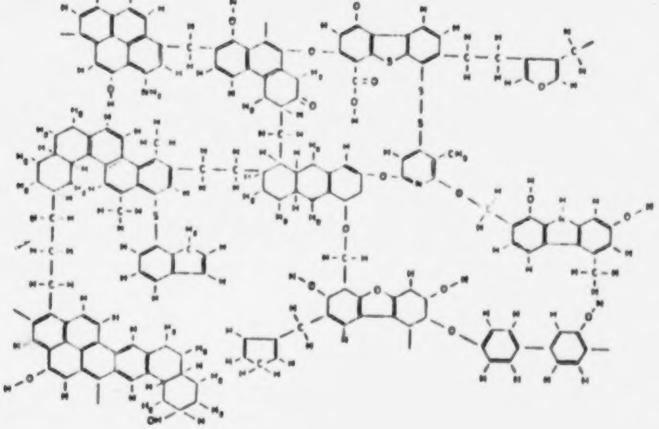
Chemical Characteristics. For a detailed characterization of contaminants in coal, and to have a better understanding of the removal methods, it is relevant to define coal in terms of its chemical composition and the important concepts of its molecular structure.

Coal consists mainly of carbon, hydrogen, oxygen, sulfur, and nitrogen. The nitrogen content may be considered as constant and amounts to 1 to 1.5 percent. Coals are predominantly aromatic in structure; 60 to 90 percent of the carbon in vitrinites is present as aromatic rings, and the percentage increases with coal rank. Chakrabaty and Berkowitz have recently suggested an adamantane-based structure for coal, but this hypothesis has received little acceptance to date with the limited evidence they have presented.(4) Cartz and Hirsch(5) showed in an X-ray diffraction study on vitrains that the structural units in bituminous coals consist of small condensed aromatic ring systems, probably 1 to 3 rings for low rank vitrains and 2 to 5 rings for vitrains with 90 percent carbon. These aromatic layers are linked to each other by C-C linkages and aliphatic groups (or possibly also by ether linkages) to form imperfect sheets which are buckled (through the presence of hydroaromatic groups) or in which adjacent aromatic-ring systems are rotated relative to each other owing to the presence of a five-membered ring. The rings and aliphatic groups form a three-dimensional array. The hydroaromatic character of coal decreases with increasing rank. The infrared spectra of bituminous vitrinites show intense bands due to aliphatic C-H vibrations and the aliphatic character of the material has also been confirmed by NMR.

Given(6) has proposed a structure for bituminous vitrinite, and Wiser,(7) in his hypothetical coal model, has shown the structures of sulfur and nitrogen compounds (see Figure 2). Wender(8) prefers to consider coals as consisting of different building blocks, as shown in Figure 3. The lignite (Coal D in Figure 3), as shown, contains fewer aromatic structures than bituminous coals contain. As a consequence, the sulfur and nitrogen compounds in lignite and lower rank coals would not exist as part of large (3 to 4 rings), condensed aromatic or heterocyclic compounds.



Bituminous Vitrinite (Given)



Bituminous Coal Structure (Wiser)

FIGURE 2. COAL STRUCTURES WITH PROBABLE SULFUR AND NITROGEN COMPOUNDS

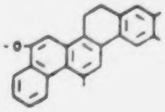
Reproduced from
best available copy.

COAL *A*

Low-volatile
Bituminous

Pocahontas No. 3 Bed, W. Va. (lvb)

	dry	maf
C	83.8	90.7
H	4.2	4.6
O	2.6	2.8
N	1.2	1.3
S	0.6	0.6
Ash	7.6	-
Volatile Matter	17.3	18.7
Btu per pound		15,660

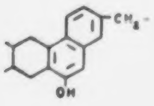


COAL *B*

High-volatile A
bituminous

Pittsburgh Bed (hvab)

	dry	maf
C	77.1	84.2
H	5.1	5.6
O	6.4	6.9
N	1.5	1.6
S	1.5	1.7
Ash	8.4	-
Volatile matter	36.5	39.9
Btu per pound		15,060

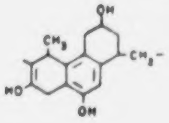


COAL *C*

Subbituminous coal

Mammoth Bed, Wyo. (Subbituminous A)

	dry	maf
C	72.9	76.7
H	5.3	5.6
O	14.8	15.5
N	1.2	1.3
S	0.9	0.9
Ash	4.9	-
Volatile Matter	41.5	43.6
Btu per pound		13,490


OH
CH₃
CH₂-
HO
OH

COAL *D*

Lignite

Lignite, Beulah-Zap Bed, N. D.

	dry	maf
C	64.5	72.6
H	4.3	4.9
O	18.0	20.2
N	1.0	1.1
S	1.1	1.2
Ash	11.1	-
Volatile Matter	40.8	45.9
Btu per pound		12,150

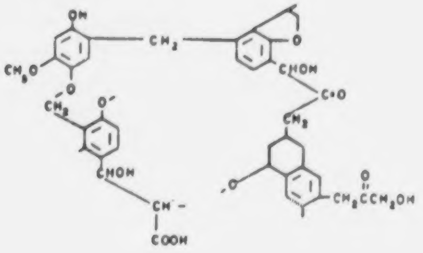

OH
CH₂
O
CH₃O
CHOH
O
C=O
CH₂
O
CH₂
CHOH
O
CH -
COOH
O
CH₂CCH₂OH

FIGURE 3. BUILDING BLOCKS OF COAL (WENDER)

The oxygen content of coal varies over a wide range, from up to 30 percent in low-rank coals (lignites) to about 1.5 percent in anthracite. The oxygen, besides decreasing the heating value of coal, forms a range of functional groups, e.g., -COOH, -OCH_3, and -OH. The phenolic hydroxyl group is the most important oxygen-containing functional group present in all ranks of coal and the only one found in bituminous coals. Coals that contain more than a few percent of oxygen are generally more reactive than coals with lesser amounts of oxygen. The reactivity is observed, e.g., in high rates of gasification, solvent extraction, and hydrogenation. Oxygen that cannot be accounted for in any other way is assumed to be in ether links or in heterocyclic systems.(9)

1.3.2. Characteristics of Petroleum or Crude Oils

Crude oil is a liquid consisting chiefly of hydrocarbons with traces of sulfur, nitrogen, oxygen, and a few impurities, such as water, sediments, and trace elements. The chemical analyses of representative American crudes from various states are shown in Table 4.

TABLE 4. ANALYSIS OF SOME REPRESENTATIVE CRUDE OILS(10)

	Percent by Weight		
Source	Carbon	Hydrogen	Impurities (include S,O,N)
Pennsylvania	85	14	1
West Virginia	84	13	3
Ohio	84	13	3
California	82	10	8
Texas	85	11	4

These data show that the percentages of carbon and hydrogen present in the crudes from all these sources are essentially the same. However, such an analysis is in a way misleading since two crudes with similar carbon and hydrogen contents could contain different hydrocarbons, e.g., Pennsylvania crude is principally paraffinic, while California crudes contain large amounts of naphthenic compounds. Some generalizations on compounds found in crudes have been made(11) and those relevant to sulfur and nitrogen contaminants in crude are: (1) all crudes contain substantially the same general structural features as the hydrocarbons, the ring systems of the hydrocarbons being replaced by hetero-ring systems.

There are two portions of petroleum crudes, the resins and asphaltenes, which are important as a source of sulfur and nitrogen contaminants. The nitrogen, sulfur, and oxygen contents of resins indicate that one or more atoms of one or more of these elements is present in each molecule. In the case of asphaltenes, the sulfur, nitrogen, and oxygen occur in concentrations equivalent to one or more heteroatom per molecule.

1.3.3. Characteristics of Tar Sands

Physical Characteristics. Tar sands should technically be called bituminous sands as the hydrocarbon which the sands contain is a bitumen (i.e., a carbon disulfide-soluble oil).(1,12) Bitumen has been classified with coal and petroleum crude as shown in Figure 1. The Athabasca tar sand is a mixture of sand, water, and bitumen, as shown in Figure 4, where the larger sand particles are coated with water and fines which in turn are coated with the bitumen film. The balance of the void volume is filled with connate water, and at times, methane or air is also present. The sand grains are packed to a void volume of about 35 percent. This corresponds to a tar-sand mixture of roughly 83 weight percent sand; the balance is bitumen and water.

The tar sands are found in Utah and in other parts of the U.S. are known by specific names, e.g., asphalt deposits, gilsonite, and grahamite. The bitumen present in these deposits has certain characteristics, appearances, and properties. The asphalts vary in consistency from plastic material to hard and brittle solids. Gilsonite is a bright, black hydrocarbon resembling glossy asphalt. The Gilsonite occurs in pure form as veins ranging from thin sheets to a maximum thickness of 2000 feet.(9) Gilsonite is hydraulically mined and transported by pipe to be converted to gasoline and asphalt. Grahamite (characterized by a low solubility in carbon disulfide) is found at many locations in the United States.

The elemental analysis of Utah asphalts, gilsonite, and Athabasca tar sands is given in Table 5.

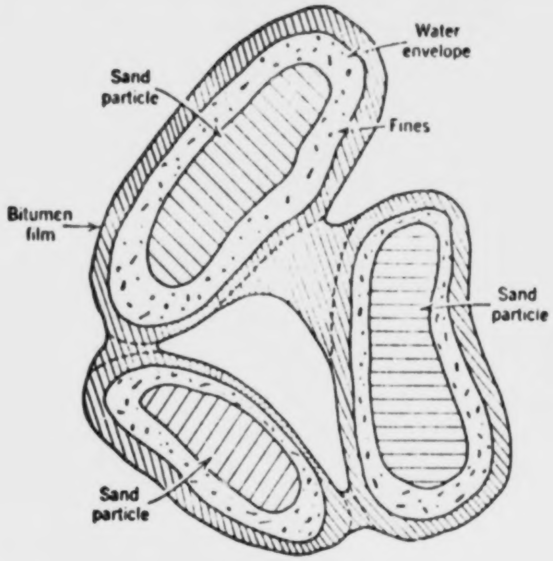

Water envelope
Sand particle
Fines
Bitumen film
Sand particle
Sand particle

FIGURE 4. ARRANGEMENT OF TAR SAND PARTICLES AND BITUMEN(12)

TABLE 5. ELEMENTAL ANALYSIS OF SOME TAR SANDS$^{(1,12)}$

Deposit	Weight Percent$^{(a)}$ Carbon	Hydrogen	Sulfur	Nitrogen
Utah asphalt	82	11	2	2-2.5
Gilsonite, m.p. 121-177 C	85-86	8.5-10	0.3-0.5	2.0-2.8
Athabasca	83.4	10.4	4.5	0.5

(a) Remainder oxygen.

Chemical Characteristics. There is paucity of information on the chemical characterization of U.S. tar sands, but the hydrocarbon constituent has been defined as bitumen. In the case of Athabasca tar sands (bitumen), each fraction of the bitumen contains large proportions of saturated carbon atoms (50 percent in solid asphalt to 75 percent in oils). Of the saturated carbon atoms within each fraction, more than 50 percent are paraffinic. The amount of naphthenic carbon in the fractions is low. In the absence of evidence for free paraffins in the bitumen, saturated constituents of the low-molecular-weight fractions appear to be single aromatic or naphthenic rings with long-chain alkyl groups. The aromatic constituents in the bituminous fractions are condensed aromatic systems ranging from 1 to 2 rings to greater than 40 rings per molecule in the asphaltenes. The asphaltenes have greater than 4 aromatic sheets containing 10 or more rings each joined by one or more alkyl rings. The asphaltene (pentane-insoluble material) constitutes about 17 percent by weight (mmf) of the bitumen.(13) It appears that the asphaltenes are due not only to chemical bonding but also to electrostatic association between the individual units.(14) The chemical analysis of Athabasca tar sands is compared with that of a coal liquid in Table 6. Some constituents of the coal liquid have lower molecular weight than the corresponding constituents in tar sand bitumen.

1.3.4. Characteristics of Shale Oil

Shale oil as obtained by the pyrolysis of oil shale in a vertical retort is a dark, viscous, organic liquid. This liquid has less than 3 percent straight-run gasoline fraction and only one-half of the total oil is distillable below 300 C at 400-mm pressure. The API gravity will be approximately 20 and the pour point around 26.7 C. This shale oil liquid as shown in Table 7 is similar in some respects to petroleum in that the refining steps and the end-use products are generally the same.(16) However, certain contaminants, e.g., nitrogen compounds, are found in larger quantities in shale oil than in most petroleum crudes, and the ratio of the olefins to paraffins is higher in shale oil. The contaminants that are finally found in processed fuels would depend on the characteristics of the source of shale

TABLE 6. CHEMICAL ANALYSIS AND MOLECULAR WEIGHTS OF TAR SANDS BITUMEN, COAL LIQUIDS, AND THEIR FRACTIONS(15)

	Mol. Wt.	C, Wt. %	H, Wt. %	N, Wt. %	O Wt. %	S, Wt. %
Tar Sands Bitumen	-	82.98	10.42	0.42	1.15	4.60
Saturates	365	86.00	14.00	--	--	--
Aromatics	460	--	--	--	--	--
Monoaromatics	360	88.55	11.36	--	--	--
Di- + Triaromatics	365	85.04	9.45	0.02	1.14	3.80
Polyaromatics	1,400	79.36	9.57	0.42	3.40	6.89
Resins	1,300	81.15	9.04	1.34	3.35	5.31
Asphaltenes	5,100	78.84	7.80	1.19	4.53	8.46
Big Horn Coal Liquids	-	89.18	8.97	0.40	1.03	0.04
Saturates	300	86.12	13.65	--	--	--
Aromatics	222	--	--	--	--	--
Monoaromatics	285	88.09	10.10	0.06	1.82	0.00
Di- + Triaromatics	220	92.38	7.13	0.01	0.80	0.15
Polyaromatics	-	84.19	6.60	0.20	7.80	0.97
Resins	380	83.84	7.09	1.62	7.15	0.30
Asphaltenes	-	87.37	6.06	1.25	4.92	0.62
Benzene Insolubles	-	--	--	--	--	--

TABLE 7. COMPOSITION OF EQUAL WEIGHT FRACTIONS DISTILLED FROM COLORADO SHALE OIL(16)

Component, percent	Fraction Composition, Percent							
	10(a) 190-270(b)	20 270-310	30 310-350	40 350-380	50 380-410	60 410-440	70 440-470	80 470-485
Polycyclic aromatics	9	9	9	10	7.5	2	2	2
Monocyclic aromatics	6	8.5	6	6.5	4.5	2	2	2
Branched olefins and cycloolefins	15	24.5	19	14	12.5	6	6	6
Straight-chain olefins	26	9	11	10.5	8.5	2.5	2.5	2.5
Branched paraffins and naphthenes	7	6	4	3	3	4.5	4.5	4.5
Straight-chain paraffins	8	8	8.5	8.5	12	3.5	3.5	3.5
Oxygen compounds	12	17	17.5	17	14	21.5	21.5	21.5
Sulfur compounds	5	4	4.5	5	5.5	7	7	7
Nitrogen compounds	12	14	20.5	25.5	32.5	51	51	51

(a) Numbers represent equal and sequential weight percent of oil removed overhead as obtained in routine distillation.

(b) Boiling point ranges of fraction, C.

oil. The source is a somewhat vaguely defined material known as oil shale, a term applied to a wide variety of laminated sedimentary rocks containing organic matter. The Colorado oil shale of the Green River Formation contains about 16 percent insoluble organic matter, the so-called "kerogen" (a term first used in relation with Scottish shales).(17) This represents about 80 percent of the total organic matter present. The remaining 20 percent soluble organic matter represents the "soluble bitumen".(18) Attempts have been made to remove the organic matter by solvents, but the yields are low because of the insolubility of kerogen; this insolubility permits one to distinguish oil shale from tar sands, which are rocks or sand formations actually impregnated with oil. The oil shales generally contain over one-third mineral matter, as shown in Table 8, and are thus distinguished from coal. Mineral constituents of Colorado oil shale, for example, include dolomite, 35 percent; calcite, 15 percent; quartz, 15 percent; feldspar, 25 percent; clay, 5 percent; pyrite, 10 percent; and minor elements listed in Table 9.

A structural model of kerogen as proposed by Yen(20) has the following features:

(1) There is little or no aromatic carbon skeleton in kerogen

(2) The bulk of the carbon structure is naphthenic, containing 3 to 4 rings. It is possible that there are clusters of rings linked by heterocyclic atoms and short-chain bridges.

(3) There are no free-end and flexible long-chain linear polymethylene structures, but polycycloparaffins could exist.

(4) The C/O atomic ratio is 18. The crosslink sites are anticipated to be largely oxygen.

(5) The difference between the structures of bitumen and kerogen is one of degree and not of kind.

(6) The structure of kerogen is a multipolymer consisting of monomers which are molecules so far identified from bitumen, as shown in Figure 5. These molecules in bitumen are steranes, triterpanes, and isoprenoids of C_{40} size. The monomers as obtained from mild oxidation are mono- and dicarboxylic acids. The ultimate analysis of kerogen is given in Table 10.

TABLE 8. MINERAL MATTER OF OIL SHALES(19)

Chemical Constituent	Analysis, percent			
	Very Low-Grade Shale (10.5 Gal/Ton)	Medium Grade Shale (26.7 Gal/Ton)	High-Grade Shale (36.3 Gal/Ton)	Very High-Grade Shale (61.8 Gal/Ton)
Raw Shale:				
SiO_2	40.9	26.1	25.5	26.4
Fe_2O_3	4.3	2.6	2.9	3.1
Al_2O_3	9.4	6.5	6.3	7.0
CaO	11.0	17.5	14.2	8.3
MgO	5.4	5.3	5.6	4.5
SO_3	0.1	0.6	1.2	1.4
Na_2O	1.8	2.6	2.7	1.9
K_2O	3.4	1.0	1.9	1.0
Spent Shale:				
SiO_2	53.27	41.90	42.36	49.19
Fe_2O_3	5.64	4.10	4.74	5.87
Al_2O_3	12.28	10.53	10.46	13.13
CaO	14.82	28.11	23.54	15.40
MgO	7.00	8.53	9.30	8.35

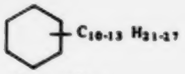
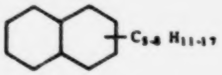
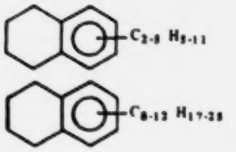
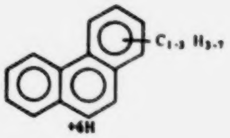
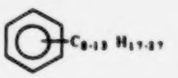
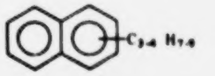
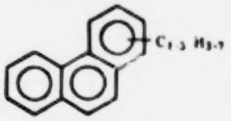
TABLE 9. PERCENTAGE OF COLORADO OIL SHALE AS MINOR ELEMENTS(19)

As	0.005	Ba	0.03	B	0.003
Cu	.008	Cr	.007	Au	.001
Pb	.09	Li	.05	Mo	.001
Mn	.08	P	.4	Se	.001
Ag	.001	Sr	.08	Tl	.7
Ti	.06	V	.06	Zn	.1

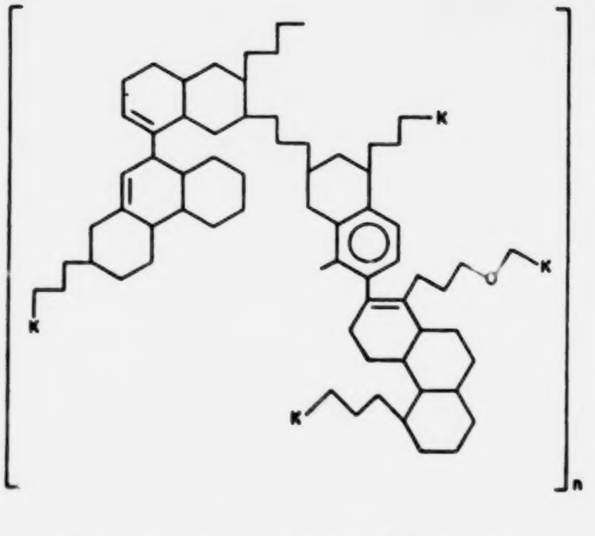
TABLE 10. TYPICAL ULTIMATE ANALYSIS OF OIL-SHALE KEROGEN(16)

	Weight Percent
Carbon	80.3
Hydrogen	10.4
Nitrogen	2.3
Sulfur	1.1
Oxygen	5.9

Principal Fragmentation Products From Controlled Pyrolysis of Kerogen Concentrate[(a)]

No.	Name	§ Formula
1	Aliphatic Hydrocarbons	n-C_{10} to n-C_{34} b-C_{10} to b-C_{36}
2	Alicyclic Hydrocarbons	
	Cyclohexane	 $C_{10-13}H_{21-27}$
	Decalins	 $C_{5-8}H_{11-17}$
3	Hydroaromatic Hydrocarbons	
	Dialkyltetralins	 $C_{2-5}H_{5-11}$ $C_{8-12}H_{17-25}$
	Hexahydro-phenanthrenes	 $C_{1-3}H_{3-7}$ +6H
4	Dialkylbenzenes	 $C_{8-13}H_{17-27}$
5	Dialkylnaphthalenes	 $C_{3-4}H_{7-9}$
6	Alkylphenanthrenes	 $C_{1-3}H_{3-7}$

(a) Subunits of kerogen identified by techniques employing micropyrolysis with pyrochromatography and mass spectrometry (MPGM method)



Generalized structure of kerogen of the Green River Formation

FIGURE 5. GENERALIZED STRUCTURE OF KEROGEN FROM COLORADO AND PRODUCTS FROM THERMAL FRAGMENTATION OF KEROGEN[(18)]

(7) Inter- and intramolecular hydrogen bondings as well as charge-transfer bonding play an important role in the structure. The kerogen is comparable in nature to a molecular sieve and it can retain small molecules present in bitumen due to van der Waals molecular forces.

Oil shale is a highly consolidated organic-inorganic system with no significant micropore structure or internal surface. The inorganic part consists of essentially nonspherical particles. The organic matter is distributed essentially interparticle rather than intraparticle and is between the particles with only a small amount of the organic matter chemically or directly bonded to the mineral constituents. The porphyrins in the kerogen may be chelated with some of the minerals. A typical kerogen molecule may be considered as a polymer with a molecular weight of well over 3000. The structure of this complex molecule consists of saturated condensed polycyclic rings with closely associated aromatic, nitrogen, and sulfur heterocyclic ring compounds that are randomly distributed.(16) This model of shale oil is consistent with the one proposed by Yen. Some kerogens show definite evidence of a benzenoid structure similar to that found in coals.

2. CHARACTERIZATION OF CONTAMINANTS IN FUELS

Characterization of sulfur, nitrogen, and trace-element contaminants in the solid and liquid fuels considered was undertaken to identify the sources of these contaminants in the fuels. After the sources of the contaminants were identified, their chemical and physical characteristics were developed relevant to contaminant removal reactions. In the case of organic sulfur and nitrogen, the discussions do not differentiate between the fuel origin of the contaminants, but instead treat them on the basis of the characteristics of either their functional groupings or parent heterocyclic compounds. In most cases, the organic sulfur and organic nitrogen contaminants are common to all of the fuels or the modified fuels (e.g., coal liquids).

2.1. Sulfur Contaminants in Fuels

The sulfur contaminants in fuels fall into two broad categories: (1) organic sulfur compounds which are found in all of the fuels and (2) inorganic sulfur compounds which are more typically found in the solid fuels, such as coal and oil shale.

2.1.1. Sulfur Contaminants in Coal/Coal Liquids

Coal contains both types of sulfur contamination. The organic sulfur is inherently bound in the organic structure of coal. The inorganic forms of sulfur are usually present outside of the coal structure as occluded mineral matter, although their distribution may be so finely disseminated that distinct phases are difficult to detect and physical separation is difficult to accomplish.

Organic Sulfur. The products from coal pyrolysis, e.g., gas, liquid, and char, all contain sulfur compounds, some of which seem to be fragments of parent compounds in coal. The organic sulfur in coal, therefore, can be considered as part of the aromatic or the aliphatic molecular structure of coal. Thus, to completely desulfurize coal, a chemical treatment is necessary. If the coal is to remain a solid, the treatment would be complicated by transport limitations that exist during reactions between a solid (coal) and gaseous or liquid reagents. The organic sulfur in coal is considered to exist in one of the following four forms:(21)

(1) Mercaptan or thiol (RSH)
(2) Sulfide or thioether (RSR')
(3) Disulfide (RSSR')
(4) Thiophene-based compounds.

There are also cyclic derivatives of these types of sulfur compounds, (e.g., R and R' may be alkyl or aryl groups; types (2) and (3) may be part of one ring system). The important organic sulfur compounds obtained from coal by pyrolysis or hydrogenation are listed in Table 11.

Inorganic Forms of Sulfur in Coal. Classical characterization of sulfur in coal differentiates between the amount of sulfur present in coal as pyrite (or sulfide) and sulfate contaminants. Organic sulfur is determined as the difference between the total sulfur value and the sum of the pyritic (or sulfide) and sulfate values.(23,24)

Sulfate Sulfur. Sulfate sulfur is usually present in coal as a result of oxidation through weathering of pyrites. Therefore, major amounts occur as iron (II) sulfate. Calcium sulfate is also known to be present as gypsum. Both are soluble in water and their concentrations in coal beds vary accordingly. Insoluble sulfate salts such as those of strontium and barium are present in coals adjacent to shales at the bottom and top of coal seams.(25) Typically they are present as cleat filling

TABLE 11. SOME ORGANIC SULFUR COMPOUNDS PRESENT IN COAL PRODUCTS

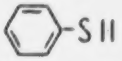
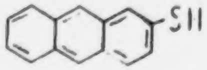
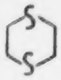
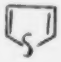
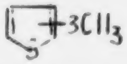
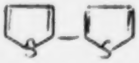
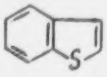
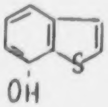
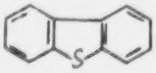
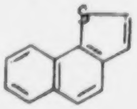
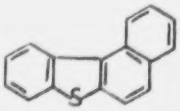
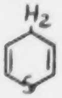
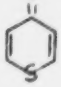
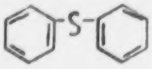
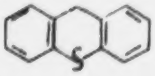
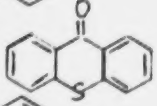
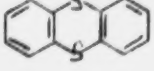
Formula	Name	Structure	B.P., C	Occurrence in(22) Coal Product
MERCAPTANS	THIOLS	(RSH)		
C_2H_5S	Ethanethiol	C_2H_5SH	35	Tar, benzole
C_6H_6S	Benzethiol		169.1	H.T. tar(a)
$C_{14}H_{10}S$	Anthrathiol			Coal oil ?
SULFIDES	THIOETHER	(RSR')		
C_2H_6S	Methylsulfide	$(CH_3)_2S$	37.3	Benzole
$C_4H_{10}S$	Ethylsulfide	$(C_2H_5)_2S$	93.1	Benzole
DISULFIDES		(RSSR')		
$C_2H_6S_2$	Methyldisulfide	$CH_3 \cdot S \cdot S \cdot CH_3$	122	Coal gas
$C_4H_4S_2$	p-Dithinin		77	Tar
THIOPHENE	DERIVATIVES			
C_4H_4S	Thiophene		84.2	Tar, benzene, coal oil
C_5H_6S	2 - Methylthiophene		112.5	Crude toluene
C_6H_8S	2-3 Dimethyl Thiophene		141.6	Tar
$C_7H_{10}S$	x_3-Trimethyl thiophene		172.6	Tar, light oil, benzole
$C_8H_{12}S$	Tetramethyl thiophene		182-184	L.T. tar(b)
C_4H_8S	Tetrahydrothiophene		121	L.T. tar, pyridine
$C_8H_6S_2$	2-2/ Bithiophene		260	Tar

TABLE 11. (Continued)

Formula	Name	Structure	B.P., C	Occurrence in Coal Product[22]
C_8H_6S	Benzo[b] thiophene (thianaphlthene)		219.9	L.T. tar, crude naphthalene, coal oil, lignite tar
C_8H_6OS	4-Thianaphthenol			Tar
C_9H_8S	2-Methylbenzo[b] thiophene		240	H.T. tar
$C_{12}H_8S$	Dibenzothiophene		331	H.T. tar, coal oil
$C_{12}H_8S$	Naphtho [2,3,6] thiophene		330	H.T. tar
$C_{16}H_{10}S$	Benzo[b] naphtho [2,1-d] thiophene			
	Naphtho [1,2-b] thianaphthene		429	H.T. tar
		CYCLIC SULFUR COMPOUNDS OF LESS IMPORTANCE		
C_5H_6S	Thiopyran(e)		30 C/12 mm	Coal tar
C_5H_4SO	Thiopyrone			
$(C_6H_5)S$	Phenylsulfide		364	Coal tar
$C_{13}H_{10}S$	Thioxanthene		340	Coal tar
$C_{13}H_8OS$	Thioxanthone		371	Coal tar
$C_{12}H_8\ S_2$	Thianthrene		296	Coal tar

(a) H.T. tar ≡ high-temperature tar.
(b) L.T. tar ≡ low-temperature tar.

minerals.(26) For freshly mined coals, the sulfate sulfur level in raw coal is usually less than 0.1 percent. In the analysis of a large number of coals, the mean value for sulfate sulfur was 0.10 percent, with minimum and maximum values of 0.01 and 1.06 percent, respectively.(23)

Pyritic (or Sulfide) Sulfur. In some raw coals, when the total sulfur is near 0.5 percent, essentially all of the sulfur is present as organic sulfur. Values greater than this are largely attributed to the presence of pyritic sulfur, although as the amount of pyritic sulfur increases so does the organic sulfur content.(23,25) Organic sulfur and pyritic sulfur comprise essentially all of the sulfur in coal.(26) Analysis of various coals of the world for total and pyritic sulfur was reported by Yancey and Greer and the value for total sulfur ranged from 0.44 to 9.01 percent. However, isolated higher values exist, e.g., 12 percent in an Iowa coal. The amount of pyritic sulfur ranges from 2.9 to 88.6 percent of the total sulfur present.(27) In American coals, the amount of pyritic sulfur ranged from 16.4 percent to 79.1 percent of the total sulfur and the mean value was 48.8 percent.(28) The reserve base of U.S. coals by sulfur content has been estimated for the eastern and western states (i.e., east and west of the Mississippi River).(29,30) It includes both the strippable and deep mine reserves. In the eastern states the reserve base was estimated to be about 203.3 billion short tons and for the western states about 234.3 billion short tons. Estimates of the sulfur content of these reserves are given in Table 12 which clearly shows that the largest reserves of low sulfur coal exist in the western states. The data did not differentiate between inorganic and organic sulfur content of these reserves but suggested that coals containing a higher percentage of an inorganic sulfur facilitated easier removal of sulfur as a percentage of total sulfur.(30)

Pyrites is the term used to describe the iron sulfides present as marcasite or pyrite geomorphs in coal. They are characterized by extreme variations in their morphology, size, and mode occurrence.(25) Those formed during the formation of the peat swamps, are considered to be syngenetic, and are the origin of the submicron-size particles closely associated with the organic matter of coal. However, nodules up to 1 meter in diameter can have similar origin. The pyrite formed subsequent to coalification (epigenetic) is present along vertical fractures and cleats and exists in a range of sizes.

TABLE 12. ESTIMATES OF THE SULFUR CONTENT IN EASTERN AND WESTERN COAL RESERVES (29,30)

Sulfur Content, Percent	Percentage of the Reserve		
	East	West	Combined[a]
≤ 1	16.2	71.4	43.8
1.1 - 3.0	27.4	16.0	21.7
>3.0	40.3	4.8	22.6
Unknown	16.1	7.8	12.3

(a) Calculated from data from Eastern and Western Reserves.

The larger pieces of pyrite are amenable to removal from the coal by physical means such as size reduction and gravity separation. The fraction of pyrite closely associated with coal is microscopic and is disseminated extensively. This form requires extensive size reduction to liberate it. Moreover, once liberated, the micron-size pyrite is often too small for gravity separation, and thus other methods, either physical or chemical, are needed to remove it from the coal.(28) A number of sulfide minerals have been reported in coals, but these occur only in small amounts.(28) They are discussed in the section on trace-element contamination in coal.

Sulfur in Coal Liquids. The coal-derived liquids obtained from a process using catalytic or noncatalytic hydrogenation refining of coal contain less than 1 percent sulfur.(31,32) When coal was liquefied without a catalyst, 14 sulfur compounds were identified; one was a disulfide and the rest were thiophene derivatives.(33) The sulfur compounds in coal-derived liquids are of an organic nature, and the pyrite sulfur present in the feed coal is readily converted to hydrogen sulfide and FeS during hydrogenation. The FeS is in suspension along with other minerals and undissolved matter and is removed with them.

2.1.2. Sulfur Contaminants in Petroleum or Crude Oils

Crudes being used today contain sulfur in varying amounts. The Pennsylvania and some mid-continent crudes contain 0.1 to 0.2 percent sulfur, while heavier California, Wyoming, and southern crudes, as shown in Table 13, contain 3 to 5 percent sulfur.(34) The mean sulfur content of all U.S. production in 1966 was 0.67 percent.(35) Crudes with a very high sulfur content exist (e.g., 7.47 percent in Oxnard, California crude or 13.96 percent in Rozel Point seepage in Utah). This wide variation in the amount of sulfur in crude is expected because of the vastly different history of the petroleum formations. The sulfur present in crude oils occurs as numerous types of organic compounds, as shown in Table 13, and also as hydrogen sulfide and elemental sulfur.(36) The concentration of sulfur compounds usually varies

TABLE 13. SULFUR PRESENT AS CONSTITUENTS INDICATED IN CRUDE OILS(34)

Field	Location	Wt. % Sulfur in Crude Oils	Distribution of Sulfur in Crude Oil, Percent of Total Sulfur						
			Residual Sulfur (Thiophene Derivatives)	R-S-R (R=Aromatic Thiophene Sulfides)	R-S-R (R=Aliphatic Sulfides)	R-S-H (Mercaptan)	R-S-S-R (Disulfide)	H_2S	Elemental S
Heidelberg	Miss.	3.75	80.3	11.7	7.8	0.0	0.2	0.0	0.0
Hawkins	Texas	2.41	73.8	14.6	11.1	0.3	0.3	0.0	0.0
Rangely	Colo.	0.76	72.0	20.3	7.7	0.0	0.0	0.0	0.0
Oregon Basin	Wyo.	3.25	68.2	13.5	15.0	1.7	1.3	0.0	0.3
Wilmington	Calif.	1.39	66.7	19.9	12.7	0.3	0.5	0.0	0.0
Midway-Sunset	Calif.	0.88	66.5	26.0	7.3	0.2	0.0	0.0	0.0
Schuler	Ark.	1.55	66.4	22.7	9.3	0.6	1.0	0.0	0.0
Agha Jari	Iran	1.36	65.7	9.6	12.8	8.5	3.4	0.0	0.0
Santa Maria	Calif.	4.99	58.2	35.5	6.1	0.2	0.0	0.0	0.0
Elk Basin	Wyo.	1.95	54.9	25.1	1.4	11.3	7.2	0.0	0.1
Wasson	Texas	1.85	52.6	13.0	11.6	15.3	7.4	0.0	0.1
Slaughter	Texas	2.01	48.8	22.5	7.5	10.8	9.2	0.0	1.2
Velma	Okla.	1.36	43.9	41.5	12.4	1.1	0.7	0.0	0.4
Kirkuk	Iraq	1.93	41.0	24.7	20.9	7.9	5.5	0.0	0.0
Deep River	Mich.	0.58	28.6	3.0	0.0	45.9	22.5	0.0	0.0
Yates	Texas	2.79	20.5	20.1	9.2	7.5	6.9	1.2	34.6
Goldsmith	Texas	2.17	17.3	11.6	9.6	10.6	8.4	0.0	42.5

directly with the molecular weight or boiling range of the fraction of petroleum being investigated. As the molecular weight of a given crude increases, the concentration of sulfur compounds increases. In many oils, the heavier fractions contain sufficient sulfur to account for at least one atom of sulfur per molecule. Although some molecular types containing two atoms of sulfur have been identified, most of the sulfur compounds in petroleum seem to contain a single sulfur atom. Thus, these heavier fractions actually consist of sulfur compounds rather than hydrocarbons.

The various types of sulfur compounds which have been positively identified in crude oils are:

(1) Mercaptans (Thiols). Alkyl thiols with both normal and branched alkyl groups, and with the thiol group in a primary, secondary, or tertiary position, have been identified. Cycloalkyl thiols containing cyclopentane rings or cyclohexane rings are also present. Aromatic thiols are not common, but benzenethiol has been identified.

(2) Alkyl Sulfides. These compounds have been found with either straight or branched structures. Cyclic sulfides having four or five carbon atoms in their ring structure are present in petroleum, but none containing less than four or more than five carbon atoms in the rings are found. The mixed alkyl-cycloalkyl sulfides and alkyl-aryl sulfides are present in low concentrations.

(3) Heterocyclic. These compounds include thiophenes, thiaindans, and thienothiophenes as the basic building blocks for sulfur contaminants found in high-boiling-point (84 to 450 C) fractions of crude. The thiophenes are the most important(36), but the thienothiophenes are not quantitatively important.(35) In the case of Wasson crude, for the 200 to 250 C boiling range, 46 sulfur compounds were identified; these included 2 thienothiophenes, 18 thianindans, 4 alkyl sulfides, and 22 benzo[β] thiophenes.(35)

2.1.3. Sulfur Contaminants in Tar Sand Oil

Ritzma, in his discussion of oil-impregnated rock deposits of Utah, considered their sulfur content as the most significant characteristic.(37) The sulfur content of the oils in Unita Basin was found to be between 0.19 and 0.82 percent. The deposits of central-southeastern Utah were found to have a sulfur content of 1.64 to 6.27 percent.

Clugston(36) has identified sulfur compounds in Athabasca tar sands, as shown in Table 14. The oils were distilled to obtain four fractions: saturates, 37 to 69 percent; monoaromatics, 13 to 21.3 percent; diaromatics, 7.1 to 15.1 percent; and polyaromatics, 10.3 to 25.6 percent. The sulfur compounds were identified in these fractions, as shown in Table 14.

TABLE 14. SULFUR COMPOUNDS IN TAR SAND OILS(38)

Oil Fraction	Total Sulfur (0.8 to 2.9 wt. %)	Mercaptan	Sulfide	Thiophene Derivative
Saturates	Trace	--	Alkyl sulfide	--
Monoaromatics	Small	--	Alkyl sulfide	Thiophene
Diaromatics	Large	--	--	Alkyl(methyl) cyclo-alkyl
Polyaromatics	Large	--	--	Alkyl-dibenzo-thiophene
Polar-polyaromatic	Large	--	--	Alkyl-dibenzo-thiophene (alkyl-small-chain; methyl abundant)

The sulfur compounds found in tar sand bitumen are thus similar to those found in coal liquids and shale oil but their concentration is higher.

2.1.4. Sulfur Contaminants in Shale Oil

It has been shown that a typical Colorado shale oil consists of 39 percent hydrocarbons (many of which are unsaturated) and 61 percent heterohydrocarbons containing oxygen, nitrogen, and sulfur. Because only 14 percent, by weight, of the original raw oil shale is valuable organic matter and only two-thirds of that is recovered, only about 10 percent of the original raw oil shale is obtained as shale oil.(16) The sulfur contaminants in raw oil shale are organic and inorganic in nature, as shown in Table 15. The total sulfur content of raw oil shale minerals from Colorado is less than 1 percent, and 33 percent of this is organic sulfur.

(1) The organic sulfur compounds to be found in shale oil would be those that withstand the retorting temperatures (500 to 700 C) of the initial recovery method. The predominant sulfur types reported are (a) heterocyclic (thiophene based) and (b) sulfides; small amounts are found as mercaptans and disulfides, as shown in Table 16.(39)

(2) Inorganic sulfur, occurs as pyrites and marcasite sulfates such as $CaSO_4$, $FeSO_4$, $MgSO_4$ in the raw shale. After retorting the oil shale the spent shale contains up to 66 percent of the raw shale sulfur as shown in Table 15. Some entrainment of spent shale and its inorganic sulfur contaminants occurs during retorting and must be separated from the recovered liquids.(40,41)

2.2. Chemical and Physical Characteristics of Organic Sulfur Contaminants in Fuels

The similarities in the types of organic sulfur compounds in the four fuel types suggest that the chemical and physical characteristics of these contaminants can be discussed as a unit rather than separately for each fuel type. The discussions relate to contaminant-removal reactions

TABLE 15. AVERAGE DISTRIBUTION OF SULFUR IN COLORADO MINEABLE-BED OIL SHALES[(a)](19)

	Percent	Remarks
Type of Sulfur Compound in Raw Shale		
Sulfide sulfur	67	As pyrite and marcasite, FeS_2
Organic sulfur	33	
Sulfate sulfur	Trace	As $CaSO_4$, $FeSO_4$, and $MgSO_4$
Total	100	
Distribution of Raw Shale Sulfur in Assay Products		
Spent shale	66	As FeS_2, FeS, CaS, and MgS with minor amounts of organic and sulfate sulfur
Oil	11	
Gas plus water by difference	23	As H_2S and possibly some SO_2 or SO_3
Total	100	

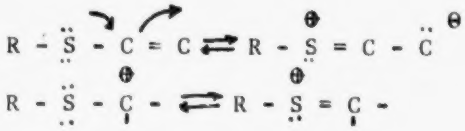
(a) Data Source: Stanfield, K.E., et al., U.S. Bureau of Mines RI 4825 (1951), Reference 41.

TABLE 16. SULFUR-TYPE COMPOUNDS IN COLORADO SHALE OIL NAPHTHA (39)

Sulfur Type	Weight Percent
Elemental	0
Thio	4
Disulfide	2
Sulfide	19
Sulfide residual (including thiophene)	75

and do not attempt to differentiate between the sources of the compounds but instead treat them on the basis of their functional groupings or parent heterocyclic compounds. However, the actual treatments used will differ depending on which constituents are present and their concentrations in each fuel type.

The processing conditions required in the conventional desulfurizing of fuels are quite severe. This could be due to the inherent stability of the C-S bond in the organic compounds. It was recognized long ago that sulfur behaved like oxygen and formed compounds such as CS_2, COS, and those equivalent to ethers and phenols. The divalent sulfur, because of the available unshared electrons, is capable of releasing electrons in conjugative interactions with electron-deficient groups or with electron withdrawing unsaturated groups as shown:



$$R - \ddot{\underset{\cdot\cdot}{S}} - C = C \rightleftarrows R - \overset{\oplus}{\underset{\cdot\cdot}{S}} = C - \overset{\cdot\cdot}{C}^{\ominus}$$

$$R - \ddot{\underset{\cdot\cdot}{S}} - \overset{\oplus}{\underset{|}{C}} - \rightleftarrows R - \overset{\oplus}{\underset{\cdot\cdot}{S}} = \underset{|}{C} -$$

Further discussion on the subject can be found in Reference 42.

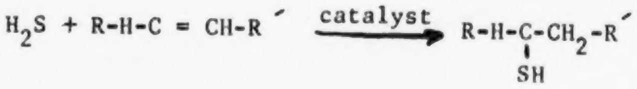
Cyclic and heterocyclic compounds containing sulfur are particularly stable. When the conjugation of a sulfur atom occurs in a ring system, it appears to be different from that in straight-chain compounds. The sulfur atom not only displays electron-releasing but also electron-accepting conjugative effects. The heterocyclic sulfur compounds have a higher resonance energy than similar oxygen compounds.

The organic-sulfur contaminants in coal liquids, shale oil, and petroleum crude can be categorized into the following four classes of compounds:

(1) Mercaptans (thiols)
(2) Sulfides
(3) Disulfides
(4) Heterocyclic (thiophene).

2.2.1. Mercaptans (Thiols)

General Formula: R-SH. The mercaptans could be naturally occurring in fuels. They can also be synthesized while the fuel is being processed. The reaction between hydrogen sulfide and an olefin gives mercaptans:



$$H_2S + R\text{-}H\text{-}C = CH\text{-}R' \xrightarrow{\text{catalyst}} R\text{-}H\text{-}\underset{\substack{|\\ SH}}{C}\text{-}CH_2\text{-}R'$$

Catalysts that have been found effective are the sulfides of metals like cobalt and nickel. These are the catalysts used in the conversion of coal or crude bottoms to more useful clean fuels. A mercaptan could also be synthesized during fuel processing by:

(1) Decomposition of a disulfide

$$RSSR \longrightarrow 2RSH$$

(2) Reaction between a phenol, alcohol, and hydrogen sulfide (commercial process, methanol to methyl mercaptan).

$$ROH + H_2S \xrightarrow{\text{catalyst}} RSH + H_2O$$

(3) Carbon disulfide hydrogenation

$$CS_2 + 3H_2 \longrightarrow CH_3SH + H_2S.$$

Physical Characteristics. The physical characteristics of mercaptans have been studied and compared with those of alcohols. The heat of formation of C-S bond is greater in the (alkyl) sulfides than in the corresponding mercaptans and is still greater in carbon disulfide.(42) The surface tension of ethyl mercaptan is less than that of alcohol. In the infrared, mercaptans have a well-defined absorption band at 3.8 to 3.85 microns. There are distinct ultraviolet bands and frequency shifts in Raman spectra. The ionization constant of mercaptans is on the order of 10^{-11}. Azeotropes have been used in the separation of mercaptans and alcohols. The boiling points, densities, and solubility in water for some mercaptans are given in Table 17.

TABLE 17. BOILING POINT, DNESITY, AND SOLUBILITY IN WATER OF VARIOUS MERCAPTANS(41)

Mercaptan	B.P., C	$d^{0}4$	S*
Methyl	5.96	0.8948	23.3
Ethyl	34.7	0.8617	6.76
Propyl	67.5	0.8617	1.96
Butyl	98.0	0.8601	0.57
Octyl	199.1	0.8500	0.004

* S = solubility, g/l, at 20 C.

Reactions and Properties. The mercaptans, besides being contaminants, are largely responsible for equipment corrosion, catalyst poisoning, and unpleasant odors. The presence of sulfur compounds in gasoline is objectionable because of odor, gum formation, corrosion, and the formation of deposits in engines. Most often sited are the mercaptans and their reaction products, alkyl disulfides and polysulfides. Mercaptans are much more acidic than corresponding alcohols.

They form addition compounds with water, nitric oxide, $AlCl_3$, $TiCl_4$, BF_4, HF, and urea. Ethane thiol forms a hydrate that is stable at low temperatures.

Decomposition. An extensive review of mercaptan decomposition is given by Reid.(43) The significant methods are:

(1) Light - Ethane thiol decomposes to ethyl disulfide, hydrogen, ethylene and higher olefins.

(2) Radiation - In an aqueous solution, the mercaptans are decomposed to a disulfide by X-ray, beta rays, and gamma rays.

(3) Thermal Cracking - Primary and secondary mercaptans decompose readily above 300 C to hydrogen sulfide and the corresponding olefin. The tertiary mercaptans decompose at lower temperatures.

(4) Catalytic Cracking - A silica alumina cracking catalyst will decompose decane thiol at 250 C to decyl sulfide and an olefin, but at 300 C, decomposition is to an olefin and hydrogen sulfide. Aromatic thiols are more difficult to decompose and at 300 C, thiophenol decomposes to give benzene and thianthrene. Some other effective catalysts proposed are phosphoric acid, sulfides of cadmium, zinc, tin, bismuth, aluminum, and iron.(43)

(5) Use of Additives - Various compounds such as cresol, furfural, terpenes, asphalt, petroleum residue, calcium cyanamide, and sodium compounds of multiring aromatics when added to petroleum promote the decomposition of the mercaptans.

(6) Catalytic Hydrogenation - With catalysts like cobalt-molybdate and nickel and molybdenum sulfides, the organic sulfur is converted to hydrogen sulfides during hydrogenation.

Oxidation. Mercaptans react with oxygen to form disulfides. The reaction below is promoted by the addition of sodium or ammonium hydroxide to the reaction mixture:

$$3C_2H_5SH + NaOH + O_2 \longrightarrow C_2H_5SSC_2H_5 + H_2O + C_2H_5SO_2Na \quad .$$

Other common oxidizing agents are iodine, hydrogen peroxide, ozone, nitric acid, potassium permanganate, sulfur dioxide, and sulfuric acid.

Mercaptans form heavy-metal complexes with mercury, copper, antimony, bismuth, and lead. The sodium and lead plumbites have been used for sweetening of sour gasolines (i.e., those that contain mercaptans).

2.2.2. Sulfides

General Formula: RSR'. The alkyl sulfides are the analogues of ethers, ROR'. The sulfides are widely distributed in nature, while mercaptans are comparatively rare. Sulfides are found in crude petroleum and distillates.(35) Sulfides have been isolated from shale oil and low-temperature tar, and the presence of organic sulfides in coal is indicated by certain specific reactions, e.g., with methyl iodide.

The sulfides found in partially treated crudes or synthetic crudes (shale oil, coal liquids) could result from the following reactions:

(1) Reaction of mercaptan and olefin

$$R'SH + RCH : CH_2 \rightarrow RCH_2CH_2SR'$$

(oxygen favors the reaction)

(2) Reaction of sulfur and hydrocarbons

$$\text{Paraffin} + S \xrightarrow{\text{heat}} \text{olefin} + H_2S$$

$$\text{Olefin} + H_2S \rightarrow \text{mercaptan}$$

$$\text{Mercaptan} + \text{olefin} \rightarrow \text{alkyl sulfide}$$

(3) Reaction of alcohols with hydrogen sulfide

$$2ROH + H_2S \xrightarrow{\text{catalyst}} R_2S + 2H_2O$$

(4) Reaction between aldehyde and a mercaptan in hydrogen

$$RCHO + RSH + H_2 \rightarrow RCH_2SR + H_2O \quad .$$

Physical Characteristics. The resemblance of sulfides to ethers is closer than that of mercaptans to alcohols. The ultraviolet and infrared absorption of sulfides has been studied. The bond energy for $C = S$, $C - S$, and $S - H$, is 177.8, 59.2, and 87.1 kcal/mole, respectively. Entropy, free energy, and heat capacities of methyl and ethyl sulfides have been determined over a wide temperature range. The alkyl sulfides form azeotropes with paraffins, olefins, and alcohols. The boiling points and densities of some sulfides are given in Table 18. The alkyl sulfides are not soluble in water.

TABLE 18. BOILING POINT AND DENSITY OF ALKYL SULFIDES (43)

Sulfide	B.P.,C	d 20/4
Dimethyl	37.3	0.8483
Methyl ethyl	66.6	0.8422
Diethyl	92.0	0.8363
Methyl propyl	95.6	0.8424
Ethyl propyl	118.5	0.8370
Methyl butyl	122.5	0.8427

Reactions and Properties. Alkyl sulfides are more reactive than ethers and readily react with many reagents.

Addition Compounds. Methyl sulfide and boron hydride form an addition compound that melts at -38 C. Ethyl sulfide dissolves in anhydrous hydrofluoric acid, forming a type of sulfonium salt, and the sulfide can be recovered by the addition of water. Methyl sulfide reacts similarly with hydriodic and hydrobromic acid. Methyl sulfoxide is an excellent solvent for sulfur dioxide.(43) Alkyl sulfides form crystalline adducts with urea. The primary product from the reaction of chlorine and bromine with alkyl sulfides and aryl sulfides is an addition compound. The aryl sulfides do not take up the halogen readily. The oxidation of sulfides to sulfoxides occurs with chlorine in the presence of water. Alkyl sulfides form addition compounds with salts of the heavy metals, e.g., platinum and mercury compounds are most numerous.

Decomposition. This usually involves the breaking of the C-S bonds. Kekūle showed that thiophene results when ethyl sulfide is passed through a hot tube. Ethyl sulfide begins to decompose at 400 C, and at 496 C, the decomposition of i-amyl sulfide, $C_{10}H_{22}S$, is complete. Phenyl sulfide, $(C_6H_5)_2S$, gives dibenzothiophene, benzene, and hydrogen sulfide. The t-butyl sulfide is converted by hydrogen sulfide into two molecules of the mercaptan. The addition compound of a sulfide, e.g., methyl sulfide with hydrogen iodide, when heated, produces a mercaptan, sulfonium iodide, and hydrogen iodide. At temperatures below 250 C under 1500 psig of hydrogen in the presence of a catalyst, the alkyl sulfide is split into a mercaptan and a hydrocarbon. Catalysts like Raney nickel and cobalt molybdate remove the sulfur as hydrogen sulfide. The cleavage of an alkyl sulfide occurs in the presence of sodium in liquid ammonia. A sulfide is decomposed by the addition of an alkyl halide; methyl iodide is most active:

$$RSR + CH_3I \rightarrow RRCH_3SI \rightarrow RI + RSCH_3.$$

Oxidation. The indirect oxidation by bromine and chlorine is an addition reaction, and occurs in two stages as follows:

$$\begin{array}{ccccc} \text{Sulfide} & \rightarrow & \text{Sulfoxide} & \rightarrow & \text{Sulfone} \ . \\ (R_2S) & & (R_2SO) & & (R_2SO_2) \end{array}$$

Nitric acid affects the first stage only, but fuming nitric acid will complete the oxidation. Potassium permanganate, ozone, hypochlorite, and hydrogen peroxide (30 percent) are efficient agents. In the oxidation of the sulfides, there is always a tendency to go beyond the sulfoxide and sulfone to a sulfonic acid. Nitric acid does not favor the formation of the sulfone but the end product could be the acid.

Metallization. Various metallization agents have been used to form metal derivatives(43), e.g., butyl lithium and mercuric acetate.

2.2.3. Disulfides

General Formula: AS·SB (A or B = alkyl or aryl group). Alkyl disulfides correspond to alkyl peroxides, RO·OR. They are stable and easily prepared in comparison with the peroxide. They are found in petroleum distillates and in partially processed coal liquids. The disulfides, like the mercaptans and sulfides, can also be synthesized during fuel processing, and some important reactions are:

(1) The oxidation of a mercaptan.
(2) The action of sulfur on organic compounds, e.g., phenols, aniline, and benzene.
(3) The sulfurization of the alkyl or aryl sulfide to a disulfide.

Physical Characteristics. The disulfides are not easily purified. They have been studied by Raman spectra, and absorption spectra that include infrared and ultraviolet. The absorption by ethyl disulfide begins at around 250 mμ . It has been reported that the rotation around the S-S bond is restricted and that dimethyl disulfide exists in cis and trans forms. Data on vapor pressure, latent heat of vaporization, heats of formation, and specific heats are available. The alkyl disulfides have been shown by diamagnetic susceptibilities to have the structure RS·SR and not $R_2S:S$. Solutions of thiols and disulfides in concentrated sulfuric acid are strongly colored. The disulfides form azeotropes with hydrocarbons, e.g., 27.5 percent dimethyl sulfide and hexane, the azeotrope boiling at 96.4 C.(43) The boiling points and densities of some disulfides are given in Table 19.

TABLE 19. BOILING POINT AND DENSITY(43) OF VARIOUS DISULFIDES

Disulfide	B.P., C	d 20/4
Methyl	109.75	1.0647
Ethyl	152.00	0.9882
Propyl	193.00	0.9599
Butyl	230.00	0.9383
Cyclopentyl	105.50	1.0617
Biphenyl	310.00	1.3530

Reactions and Properties. Disulfides, besides undergoing thermal decomposition and oxidation, are reduced and undergo hydrolysis.(43)

Decomposition. The S-S bond in a disulfide is reactive. Aryl disulfides can be decomposed by ultraviolet light. Like the peroxides, the disulfides generate free radicals. The aliphatic disulfides are not as efficient as the aryl disulfides in this respect. Benzyliodide combines with benzyl disulfide and mercuric iodide to give $(C_6H_5\cdot CH_2)_3SI\cdot HgI$. Ethyl disulfide gives a sulfonium salt. These reactions suggest that the S-S bond is broken.

Aliphatic disulfides are unstable at high temperatures, and the product of pyrolysis will be a mixture of mercaptan, monosulfide, and hydrogen sulfide. Aromatic disulfides are more stable, and one of the products on thermal decomposition is a mercaptan. In the case of diphenyl sulfide decomposition, many products have been reported, e.g.,

Diphenyl disulfide $\xrightarrow{270\text{-}300\ C}$ monosulfide, dibenzothiophene, thiophenol, thianthrene

In general, the aromatic disulfides when decomposed by metal salts (e.g., aluminum chloride) or by a metal (e.g., copper) form other aromatic derivatives that include the thiophene structure. Decomposition can also be achieved by using microorganisms.

Reduction. The disulfides can be completely reduced to a mercaptan. A mixture of a disulfide and mercaptan can be considered as an oxidation-reduction buffer, analogous to the well-known acid-base buffers. Some reagents which convert sulfides to mercaptans are sodium hydrosulfide, sulfide, disulfide, or polysulfide. Higher alkali polysulfides may convert mercaptans to disulfides and even add sulfur to the alkyl disulfide. The presence of a mercaptide is believed to act as a catalyst. Reduction can also be achieved with glucose, sodium arsenite, or lithium aluminum hydride, or by hydrogenation over a molybdenum sulfide.

Oxidation. A disulfide is an intermediate in the oxidation of a mercaptan and on further oxidation produces acids. The common oxidants used are nitric or sulfuric acid, chromate, permanganate, hydrogen peroxide, and oxygen containing nitrogen oxides. Chlorine forms sulfuryl chlorides which can be separated from other hydrocarbons by a hot alkali wash. In the presence of bromine, a disulfide appears to form an addition product.

Hydrolysis. The disulfides are split during alkaline hydrolysis:

$$(CH_3)_2S_2 + 2NaOH \rightarrow CH_3S\ Na + CH_3SO\ Na + H_2O.$$

Some disulfides, e.g., t-butyl are not affected by alkali. Thus, cleavage seems to depend on the presence of a hydrogen atom on the carbon linked to the sulfur.

Other Reactions. Disulfides form complexes with salts of platinum, mercury, gold, silver, and indium. Copper napthanate reacts with disulfides to form complexes. Mercuric chloride forms mercuric compounds with some aromatic disulfides.

2.2.4. Heterocyclic (Thiophene)

Sulfur forms many heterocyclic compounds that consist of three-, four-, or five-member rings. The large size of the sulfur atom may account for the fact that ring compounds with five members are more common than those with six members. When considering fuel contaminants, the five-member ring compound thiophene and its derivatives are the most important. Thiophene was discovered in coal tar in 1883.(44) In 1899, Charistschoff reported that Grosny crude contained 1 ppm thiophene. The inherent stability of thiophene makes its removal a challenge. Reid(43) and Hartough(44) have extensively discussed the basic chemistry of thiophenes. The resonance energy of thiophene is 31 kcal/mole and that of benzene is 36 kcal/mole, which helps explain its aromaticity.

The synthesis of thiophene during fuel processing is accomplished by ring-closure reactions that could occur by

(1) Joining a C_4 alkane unit at the 1,4-carbons by a sulfur atom
(2) Reactions akin to the production synthesis of thiophene, e.g., by the reaction of butane and sulfur at high temperatures
(3) Reaction of an olefin and sulfur at 600 C
(4) Decomposition and cyclization of a disulfide.

Physical Characteristics of Thiophene. Thiophene is a colorless liquid, insoluble in water, having an odor somewhat like benzene when highly purified. In general, the derivatives of thiophene have odors fairly similar to those of their benzene isologues, i.e., 2-thiobenzaldehyde and benzaldehyde. The monosubstituted thiophene derivatives usually boil at higher temperatures than the corresponding benzene derivatives. The thiophene compounds, however, are usually not as thermally stable as benzene. The molecular structure and spectroscopy of thiophene and its derivatives was published in API Project 44 reports.(35) Some physical properties of thiophene and methyl thiophene that are related to contaminant removal are given in Table 20.

TABLE 20. BOILING POINT, DENSITY, AND FREEZING POINT OF THIOPHENE AND SOME DERIVATIVES(44)

Compound	B.P., C/900mm Hg	d_4^{30}	Freezing Point, C
Thiophene	89.7	1.0542	-38.30
2-methyl-	118.4	1.0086	-63.50
3-methyl-	121.3	1.0110	-68.9

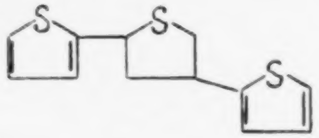
Reactions and Properties. Thiophene and its derivatives exhibit certain characteristic chemical reactions.(43,44) It is unnecessary to draw a chemical distinction between thiophene and benzene other than to say that they are distinct chemical compounds to be compared only because both happen to be aromatic compounds. Thiophene cannot easily be compared with pyrrole and furan since there are many reactions of these that fail with the thiophenes. The following reactions may be used to remove thiophenes from fuels.

Catalytic Hydrogenation and Hydrogenolysis. Thiophene poisoning of hydrogenation catalysts for benzene was first mentioned in 1912 when benzene containing 0.01 mg of thiophene per gram of benzene could not be hydrogenated over platinum.(44) Thiophene can be successfully hydrogenated to tetrahydrothiophene without the breakage of the C-S bond. The commonly used catalysts are cobalt molybdate or sulfides of cobalt and molybdenum. Molybdenum disulfide at 200 C and 200 atm of hydrogen pressure promotes the hydrogenation of thiophene to the tetrahydrothiophene in yields of 52 percent. The other products are butyl sulfide (11 percent) and butyl mercaptan (6 percent).(44) Higher temperatures bring about the breakage of C-S bond, and catalysts like nickel-tungsten sulfide, cobalt tetracarbonyl, and rhenium sulfide have been used. In this case, the sulfur is removed as hydrogen sulfide and butane is produced.

Decomposition. Chemically, thiophene is less stable than benzene. Ring rupture with evolution of hydrogen sulfide begins to take place at about 200 C in the presence of silica-alumina-type cracking catalysts. In the presence of 100 percent orthophosphoric acid, some ring rupture is observed at the boiling point, and with sulfuric acid, polymerization occurs with evolution of sulfur dioxide. Thallous hydroxide decomposes thiophene to give thallous succinate and thallous sulfide. Potassium causes ring rupture and potassium sulfide is formed, while sodium is inactive. Ozone, when bubbled through a suspension of thiophene in water, forms an ozonide. Thiophene undergoes autoxidation in light and is decomposed to sulfuric and oxalic acids.

Halogenation and Decomposition. Chlorination of thiophene in a liquid phase can be carried out at low temperatures, ranging from -30 C to 84 C. Both substituion and addition to the thiophene nucleus take place. In general, the polychlorothiacyclopentanes (polychloro-thiophenes) are stable below 150 C and can be distilled under vacuum without decomposition. These compounds can be decomposed by pyrolysis, alcoholic caustic, solid potassium hydroxide, hot potassium carbonate, or zinc dust in water and alcohol. The bromothiophenes undergo mercuration, metallization with sodium, nitration, sulfonation, acylation, and typical Grignard reactions. The iodination of thiophene can also be accomplished by using iodine and mercuric oxide.

Alkylation. Direct alkylation of thiophene can be accomplished easily by reaction of certain branched-chain olefins with thiophene in the presence of mineral acids. Isobutylene and thiophene react to form butylthiophenes and di- tertbutylthiophenes. With activated clays, dilute sulfuric acid, and phosphoric acid, thiophene polymerizes to a trimer and a pentamer. The trimer has been shown to have the structure



Concentrated sulfuric acid and aluminum chloride produce amorphous red polymers of high molecular weight. Alcohols can also be used as the source of alkyl groups if stannous chloride is used as a catalyst:

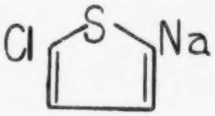
$$C_6H_5CH_2OH + \text{thiophene} \xrightarrow{SnCl_2} \begin{array}{l}\text{2 benzylthiophene}\\ \text{2,5 dibenzylthiophene.}\end{array}$$

Aldehydes, especially formaldehyde, react with thiophene in the 2,5 positions to produce polymers when the reaction is catalyzed by strong mineral acids. Some aldehydes such as benzaldehyde can be condensed with thiophene in the presence of activated clays.

Oxidation. Thiophene and hydrogen peroxide form a sulfane as the intermediate product and then ring rupture occurs to give fumeric acid (HOOCHCHCOOH). The highly substituted and condensed thiophenes form stable sulfanes.

Sulfonation. Selective sulfonation of thiophene with 96 percent sulfuric acid was the method first used to show the presence of thiophene in coal tar. For the purpose of identification and isolation of thiophene, the sulfonic acid obtained was converted to the lead salt and thiophene was then recovered. However, sulfonation can lead to polymerization as well.

Metallization. The reaction of mercuric compounds, e.g., mercuric chloride and mercuric acetate, with thiophene occurs readily. These salts have been used for the concentration and purification of thiophenes, since the highly insoluble mercury salts can be separated easily. Lithium and sodium derivatives are easily prepared. Most lithium and sodium derivatives are prepared by a transmetallization reaction involving thiophene or a substituted thiophene and an alkyl or aryl lithium or sodium. While lithium does not react with 2-chlorothiophene dissolved in ether or benzene, sodium reacts at 60 to 80 C to give a sodium derivative, and at 20 to 30 C, gives a 5-chloro-2-sodium derivative:



2.3. Nitrogen Contaminants in Fuels

The nitrogen contaminants in fuels have not been characterized as well as the sulfur contaminants. In general, the nitrogen is considered to be of organic origin. Inorganic-nitrogen sources outside of some rare instances do not apparently exist.

2.3.1. Nitrogen Contaminants in Coal/Coal Liquids

Coal contains nitrogen in the form of organic compounds which are part of its organic structure. Traces of inorganic nitrogen have been found, as nitrates, in the low-temperature ashes of some western coals, but its origin is postulated as part of the ashing process, and is not believed to be in the raw coal.

It is quite difficult to describe the state of organic nitrogen in coal. Hauck(45) reiterates that "little is known with certainty about the nitrogen forms in coal". In the process of identification of the nitrogen compounds in coal, the compounds are altered by thermal or chemical effects used in their isolation, so that the nitrogen compounds ultimately determined may not be representative of the original compounds in coal. Use of a mild selective solvent extraction has partially circumvented this problem. This technique(46-50) has been carried out, but some coal pretreatment is also involved. In another approach, the nitrogen compounds are identified in coal degradation products (e.g., coal tars). Then, on the basis of the nitrogen compounds identified in the products, postulates are made as to the type of nitrogen compound originally in coal.

In 1925, Francis and Wheeler(50) concluded that nitrogen in coal was aromatic in nature. This was proved conclusively when, by coal/nitrogen analysis, it was shown that nitrogen occurred in pyridine, picoline, quinoline, and nicotine structures.(48) The nitrogen content of U.S. coals of different ranks is given in Table 21.

TABLE 21. NITROGEN CONTENT OF U.S. COALS(50)

Coal	Maf coal, percent
Lignite	1.0
Subbituminous	1.2 - 1.7
High volatile C bituminous	1.6 - 2.1
High volatile B bituminous	1.7
High volatile A bituminous	1.6 - 1.9

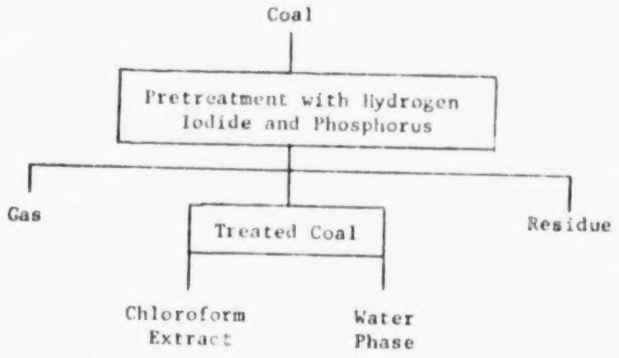
Coals contain 10 to 30 times the amount of nitrogen present in wood. It has been shown in numerous studies that soil humus, humic acid, and peat, i.e., precursors of coal, contain the nitrogen compounds shown in Figure 6. Thus, some complicated mechanisms concentrate the nitrogen of the wood to the levels found in coal, since the nitrogen content of younger coal (peat) is less than that of bituminous coal, as shown in Table 21.

Coals that are treated with hydrochloric or sulfuric acid produce an extract that contains up to 78.5 percent of the nitrogen present in young coals (peat), but only 2.64 percent of that in anthracite. Thus it is concluded that in older coals (anthracite), the nitrogen compounds are neither basic nor are they present as reactive species, but instead are linked to other groups.(51)

Another scheme for the determination of the distribution of the nitrogen bond types is given in Table 22.(46) The nitrogen bond types isolated in water and chloroform extracts and in the residue were determined. A reductive pretreatment with hydrogen iodide and phosphorus was carried out to enhance coal extraction, but this pretreatment could alter the coal constituents, and in this specific study, a gas was produced which contained 26 percent of the coal nitrogen.

Nitrogen compounds isolated in the tarlike products of coal pyrolysis have been identified by many workers.(51-53) The nitrogen compounds are aromatic in nature and could be derivatives of those shown in Table 23. The derivatives could be alkyl substituted or combinations of the compounds in Table 23 to give aza coronene, nitrites, quinoline, and indole structures. Other compounds, e.g., acetonitrile and benzonitrile,

TABLE 22. BITUMINOUS COAL TREATMENT AND DETERMINATION OF NITROGEN BOND TYPES(44)


Coal
Pretreatment with Hydrogen Iodide and Phosphorus
Gas
Treated Coal
Residue
Chloroform Extract
Water Phase

Extract	Nitrogen Bond Types	Percent N in Coal
Water	Purine bases, urea structures, aminoacids, peptides	35
Water	Carbazole structures	10
Water	Cyclic bases, phenylamines	3
Chloroform	Nonbasic N-compounds, fatty amines, hydrophobic basis	23
Residual nitrogen		3
Nitrogen in gas on pretreatment		26
	Total	100

TABLE 23. NITROGEN COMPOUNDS AS BUILDING BLOCKS FOUND IN COAL TARS

- Pyrroles
- Pyridines
- Anilines
- Indoles
- Quinolines
- Fluoranthene
- Carbazoles
- Acridines
- Perylenes
- Coronene

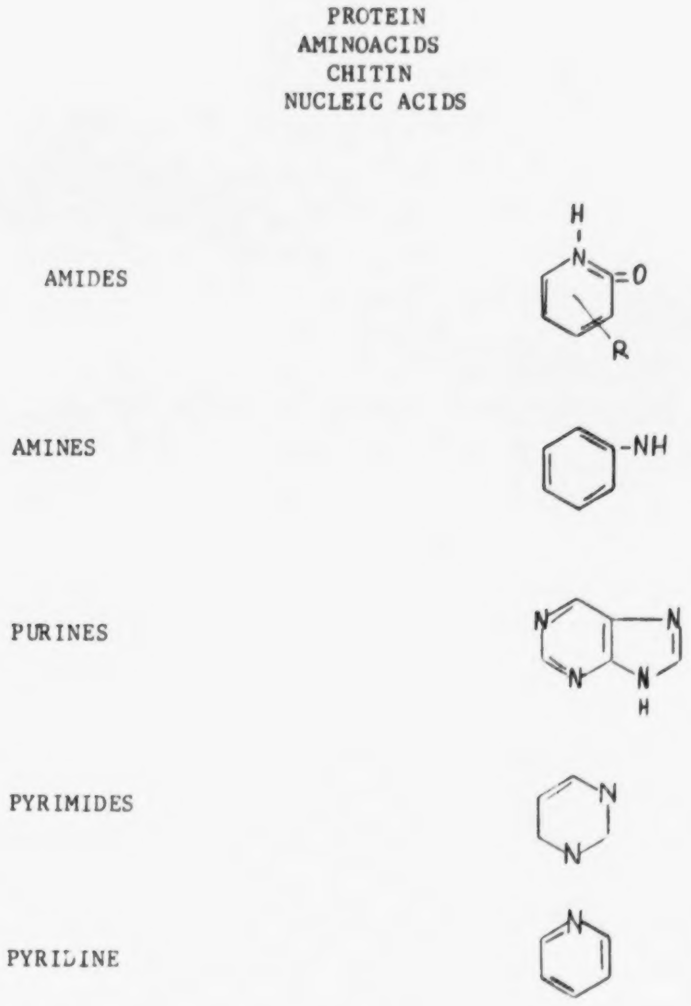

PROTEIN
AMINOACIDS
CHITIN
NUCLEIC ACIDS
AMIDES
H
N
=O
R
AMINES
-NH
PURINES
N
N
N
N
H
PYRIMIDES
N
N
PYRIDINE
N

FIGURE 6. NITROGEN COMPOUNDS EXTRACTED FROM COAL PRECURSORS (Humic Acids, Peat) (51)

have also been identified which probably were produced from the degradation of larger aromatic compounds. Compounds identified in coal tar have a molecular-weight range of 167 to 301, as shown in Table 24.(53) In a more recent study twice as many of the structural types than previously reported in literature have been determined, but the nitrogen compounds identified all fall into the type of compounds shown in Table 24.(53)

2.3.2. Nitrogen Contaminants in Petroleum

Nitrogen contaminants in petroleum occur in amounts ranging from a trace up to slightly less than 1 percent, and are primarily organic compounds. The nitrogen compounds found in crude oil fall into two main categories, basic and nonbasic, as shown in Figure 7. The significance of the basic and nonbasic nature is discussed later in the section on processing of nitrogen-rich fuels. The nitrogen compounds are generally concentrated in the heaviest portion of crude oil, as shown in Table 25. When a petroleum is separated into oils, resins, and asphaltenes, the nitrogen compounds are found to be concentrated in the latter two classes. The types of nitrogen compounds found in petroleum are shown in Table 26.

The nitrogen compounds found in shale oil and coal tar may suggest compounds likely to be found in petroleum. Compounds like pyridine, quinoline, isoquinoline, dihydropyridine, pyrroles, and nitriles which have been found in shale oil and carbazoles, indoles, benzonitrile, amides, and others which have been found in coal tar, are also reported in petroleum crudes.(56,57)

Porphyrins, another class of nitrogen-containing compound, are also associated with the high-boiling portion of crude oil. They also include nickel or vanadium in their structure. The structure of a vanadium prophyrin is shown in Figure 7.

TABLE 24. NITROGEN COMPOUNDS IN CREOSOTE OIL AND COAL TAR PITCH(52)

Structural Types	Molecular Weight	Total Weight,[a] percent	Total Weight,[b] percent
Nitrogen Compounds			
Carbazole	167	4.6	0.1
Acridine	179	2.5	0.8
4H-Benzo[def]carbazole	191	1.6	0.6
Dibenz[cd, g]indole	203	1.6	1.6
11H-Benzo[a]carbazole	217	3.6	1.6
Benz[c]acridine	229	1.3	1.0
1H-Anthra[2,1,9-cde]indole	241	0.7	--
Indeno[7,1-ab]acridine	253	.6	1.4
Dibenz[b,h]acridine	279	.1	0.5
9H-Phenathro[4,5-abc]carbazole	291	Trace	--
X-Azabenzo(ghi)fluoranthene	227	--	0.6
Z-Azabenzo(ghi)perylene	277	--	0.6
Anthra(1,9-ab)carbazole	303	--	0.4
X-Azacoronene	301	--	0.1
Total		15.0	7.7

(a) Creosote oil.

(b) High-temperature coal tar.

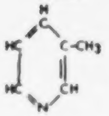
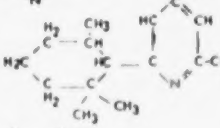
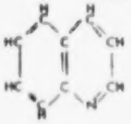
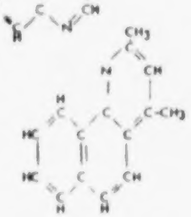
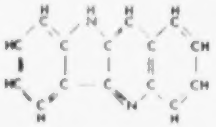
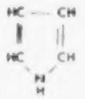
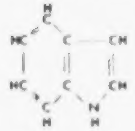
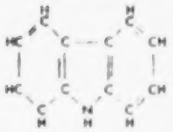
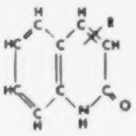
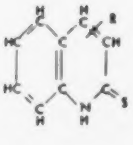
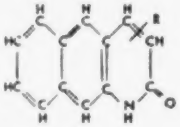
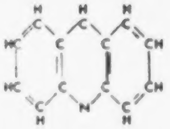
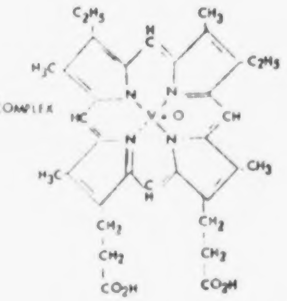
Name	Structure	Found In
	Basic	
3-METHYLPYRIDINE		Gasoline
4,6-DIMETHYL (2,6,6-TRIMETHYLCYCLOHEXYL) PYRIDINE		Kerosine
QUINOLINE		Kerosine
2,4-DIMETHYLBENZO[h] QUINOLINE		Gas oil
INDOLOQUINOLINE		Gas oil (Possibly cracked)
	Nonbasic	
PYRROLE		Not found (Possible in gasoline)
INDOLE		Not found (Possible in kerosine)
CARBAZOLE		Gas oil
	Nonbasic - Continued	
2-QUINOLONE		Gas oil
2-THIOQUINOLONE		Gas oil
BENZ-2-QUINOLONE		Gas oil
ACRIDINE		Gas oil
VANADIUM-PORPHYRIN COMPLEX		Heavy gas oil Residual

FIGURE 7. REPRESENTATIVE BASIC AND NONBASIC NITROGEN COMPOUNDS IN PETROLEUM PRODUCTS(55)

TABLE 25. DISTRIBUTION OF NITROGEN IN CRUDE OIL(54)

Field	Nitrogen in Crude Oil, percent by weight	Percentage of Nitrogen in Residuum
Schuler, Ark.	0.06	88
Heidelberg, Miss.	0.11	106
Deep River, Mich.	0.12	91
Midway-Sunset, Calif.	0.58	85
Wilmington, Calif.	0.65	86
Velma, Okla.	0.27	89
Yates, Texas	0.16	88
Ch[illegible], Colo.	0.03	100
Dallas, Wyo.	0.28	96
Derby, Wyo.	0.25	96
Pilot Butte, Wyo.	0.22	95
Keri, Greece	0.17	94
Circle Ridge, Wyo.	0.23	96
Winkleman Dome, Wyo.	0.23	91
Sage Creek, Wyo.	0.28	93
Steamboat Butte, Wyo.	0.16	88

TABLE 26. NITROGEN COMPOUNDS IN PETROLEUM(54)

Types of Nitrogen Compounds Found		
In Crude Oil		
By Identifying Individual Compounds	Only as Type Identification	Only in Processed Fractions
Carbazoles	Pyrroles	Anilines
Pyridines	Indoles	Phenazines
Quinolines	Isoquinolines	Nitriles
Tetrahydroquinolines	Acridines	
Dihydropyridines	Porphyrins	
Benzoquinolines		

2.3.3. Nitrogen Contaminants in (U.S.) Tar Sand/Oil

A detailed characterization of the tar sands has shown that the tar sand oils can be separated into acids, bases, nonbasic nitrogen, and saturated and aromatic fractions.(58) The elemental analysis of tar sands is given in Table 5, which shows that Utah asphalt and gilsonite have a nitrogen content of 2 to 2.5 and 2 to 2.8 weight percent, respectively, compared to 0.5 weight percent for Athabasca tar sands.

The elemental analysis of bitumen from P. R. Springs, Utah, is given in Table 27. The samples have the carbon-hydrogen atomic ratio of 0.637 which suggests that the bitumen is of average composition and the sulfur-nitrogen weight ratios are less than 1 which is similar to petroleum crudes. The oxygen content (2.59 percent) is high compared with that of other fuels.

A gross comparison of the composition of P.R. Springs bitumen with petroleum residues is shown in Table 28 where the nonhydrocarbon content (includes acids, bases, and nonbasic nitrogen) of the P. R. Springs bitumen is high (46.2 percent), second only to Gach Saran residue. Also it is known that the P. R. Springs bitumen contains 30 to 50 percent material in the 275 to 500 C boiling range which is absent in the petroleum residues. This suggests that a comparable initial-boiling-point residue of the P. R. Springs bitumen with that of petroleum residues would have an unusually high content of nonhydrocarbons.

The analysis of the nonhydrocarbon (46.2 percent) content of P. R. Springs is shown in Table 29. The bitumen acid fraction consists of carbazoles (pyrrolic N-H) that are common with coal liquids and petroleum residues. The amide fraction is greater than that in other fuels.

2.3.4. Nitrogen Contaminants in Shale Oil

A characteristic of shale oil is its high nitrogen content as compared with that of petroleum. The nitrogen contents of the distillation fractions of a Colorado shale oil containing about 1.6 total weight percent nitrogen are given in Table 30. The data in the table show that the nitrogen of the distillate fraction increases with the temperature of the cut. The residuum fraction (b.p. > 430 C) contains 62 percent of the total nitrogen.

TABLE 27. P. R. SPRINGS, UTAH, BITUMENS (TAR SAND OILS)(58)

Property	Sample A This Study (Core)	 B Main Canyon Seep	 C Core 79 to 83 ft	 D Core 137 to 141 ft	 E Outcrop Sample No. 69-13E	 F Outcrop Sample No. 67-1A
Specific gravity 60/60	0.998	0.974	0.995	1.004	1.016	0.969
API gravity	10.3	13.8	10.7	9.4	8.3	14.5
Elemental analysis, weight percent						
Carbon	84.44				80.0	86.0
Hydrogen	11.05				9.5	10.9
Sulfur	0.75	0.34	0.33	0.40	0.45	0.36
Nitrogen	1.00	0.77	0.88	1.08	1.0	0.67
Oxygen(a)	2.59					
C/H (atomic ratio)	0.637				0.702	0.657
S/N (weight ratio)	0.75	0.44	0.38	0.37	0.45	0.54

(a) Determined by difference.

TABLE 28. GROSS COMPOSITION OF SELECTED BITUMEN (TAR SAND OIL, CRUDE OILS)(58)

Components	Components of Residue Sample, Percent P.R. Spring >225 C(a)	 Wil-mington >485 C	 Red Wash >545 C	 Recluse >750 C	 Gach Saran >675 C	 Prudhoe Bay >675 C
Acids	15.4	10.7	6.0	5.9	12.1	10.0
Bases	12.3	13.3	10.2	8.3	14.2	15.7
Nonbasic nitrogen	18.5	20.4	10.8	17.4	23.2	12.6
Saturated hydrocarbons	25.7	18.4	51.8	40.8	25.6	32.9
Aromatic hydrocarbons	24.9	35.1	10.9	24.8	18.7	23.4
Recovery	96.8	97.9	94.4	97.2	93.8	94.6

(a) Boiling point of the residue sample.

TABLE 29. NONHYDROCARBON CONCENTRATE[58]
P.R. SPRINGS BITUMEN

Fraction	Weight % of Bitumen	Molecular Weight	Weight Percent of Fraction				
			Carbolic Acids	Phenols	Carbazoles	Amides	Unidentified by IR
Acids I	4.8	1240	4	9	34	40	13
II	2.2	1161	28	20	18	33	1
III	4.0	853	60	6	7	10	17
IV	4.4	(850 est.)	39	4	17	9	31
Bases I	2.0	855			trace	67	33
II	1.5	(900 est.)				55	45
III	8.8	952				17	83
Nonbasic nitrogen I	10.3	982			32	55	13
II	8.2	(982 est.)			17	51	32
			Weight Percent of Bitumen				
Total	46.2		4.9	1.3	7.7	20.1	12.2

TABLE 30. NITROGEN DISTRIBUTION IN SHALE-OIL FRACTIONS(59)

Fraction	Boiling Range, C	Amount in Shale Oil, volume percent	Nitrogen in Fraction, weight percent
Naphtha	Below 200	3	1.17
Light distillate	200-310	16	1.24
Heavy distillate	310-430	34	1.60
Residuum	Above 430	47	2.04

Poulson(60) has reviewed the characterization of shale oils and concludes that the principal nitrogen-containing species are pyridine- and pyrrole-type compounds. In shale oils with a boiling range of 329 to 583 C, a nitrogen concentrate containing 3.79 percent nitrogen was obtained.(61) This oil contained compounds having about 15 to 30 carbon atoms, and about half of the compounds contained nitrogen. The nitrogen compounds consisting of pyridines, dihydropyridines, indoles, and quinolines comprised over half the nitrogen compounds in this oil. Much of the remainder consisted of compounds having one or more saturated rings condensed with these compounds. In addition, smaller quantities of compounds having three or more aromatic rings were present. The multiring compounds contain a greater number of substituents, e.g., OH and alkyl. About twice as many pyridines as dihydropyridines, indoles, and quinolines were found. Pyrroles were present in small amounts in the heavier fractions. The pyrroles could have been lost due to the high temperature of retorting. The distribution of nitrogen-ring compounds in shale oil is given in Table 31. About 40 percent are multiring compounds.

TABLE 31. NITROGEN COMPOUNDS IN SHALE OIL (59)

	Percent
One-ring compounds	35
Two-ring compounds	25
Multiring compounds	40

The nitrogen in the different distillate fractions of shale oil is evenly distributed. The decrease in the carbon-hydrogen ratio is such that the relationship of these elements in the average molecule for each of the cuts is about C_nH_{2n-11}. Thus the increase in molecular weight is due principally to the addition of methylene groups to the aromatic heterocyclic nucleus. In shale oil with a boiling range of 329-593 C, the alkyl and cycloalkyl pyridines comprise 35 percent of the nitrogen compounds in the oil based on single-ring aromatics in the molecule. The bicyclic, e.g., indoles and quinolines, make up 25 percent, and the remaining are multiring compounds, many of which also contain oxygen.(61)

When chlorophyllin was used as a kerogen model compound to study the probable precursors for pyrroles in shale oil pyrolysis, the distribution of nitrogen compounds formed was comparable to that in shale oil.(59)

A shale-oil light fraction with a boiling range of 204 to 316 C was found to contain over 43 percent of its nitrogen compounds as alkyl pyridines and only 4 percent as pyrroles and indoles, as shown in Table 32. The nitrogen compounds were classified as weak bases, very weak bases, and nonbasic (pyrroles).

Other nitrogen compounds that occur in small amounts in shale oil are the amides, arylamides, and nitriles.(59, 63-65)

Porphyrins, another source of nitrogen contaminants which have been extracted from shale oils undergo pyrolysis similar to chloraphyllin. They are discussed in more detail in the section on trace elements.

2.4. Chemical and Physical Characteristics of Organic Nitrogen Contaminants in Fuels

The similarities in the kinds of organic nitrogen compounds in the four fuel types suggest that the chemical and physical characteristics of these contaminants can be discussed as a unit rather than separately for each fuel type. The discussions relate to contaminant-removal reactions and do not attempt to differentiate between the sources of the compounds, but rather treat them on the basis of their functional groupings or parent heterocyclic compounds.

The nitrogen contaminants concentrate in the heavier fractions of liquid fuels. Nitrogen removal from the lighter fractions of petroleum

TABLE 32. NITROGEN TYPE ANALYSIS OF SHALE OIL DISTILLATE (204 TO 316 C)(63)

Nitrogen Type	Percent of Total Nitrogen
Weak bases (pKa = +8 to +2)[a]	
Alkylpyridines	43
Alkylquinolines	22
Very weak bases (pKa = +2 to -2)	
Alkypyrroles (N-H)	10
Alkylindoles (N-H)	9
Cyclicamides (pyridones, quinolones)	3
Anilides	2
Unclassified	7
Nonbasic (pKa < -2) corrected for pyrroles and indoles	4

(a) pKa is the log of 1/Ka where Ka is the dissociation constant of the compound.

crudes is rapid at mild conditions, whereas, under conventional hydrogen treatment procedures, extreme pressures and temperatures are required to remove the nitrogen from residues.

Nitrogen, which has five-valence electrons, forms heterocyclic compounds analogous to cyclohexane. Two valence electrons are involved in the formation of covalent bonds to the adjacent carbon atoms in the ring; one valence electron is involved in the bond to a hydrogen atom or an alkyl or alkyl group, and two electrons (the "lone pair" electrons) are not involved in bond formation. Like ammonia, which is saturated with respect to hydrogen, but not to hydrogen ions, the organic nitrogen compounds can thus form an ammonium ion by the addition of a proton. Saturated nitrogen heterocyclic compounds (e.g., piperidine) show similar characteristics.

The most abundant nitrogen compounds fall into the following two categories, basic or nonbasic (see Figures 6 and 7 for structures)(22):

Basic	Nonbasic
Methylamine	Pyrroles
Pyridine	Indoles
Quinoline	Carbazoles
Piperidine	Phenazines
Indole-quinoline	Benzonitriles
Acridine	Benzamides

The properties of these compounds are discussed with emphasis on breakage of the C-N bond, the removal of nitrogen from the molecule or of the nitrogen-containing molecule as a complex. Many individual nitrogen compounds have been identified in fuels. Over 130 individual nitrogen-base hydrocarbons have been identified in low-temperature bituminous coal tar, but they are all derivatives of the compounds listed above.(66) In the following, the more important characterisitics of these compounds are covered under each parent compound. The pKa values are also given for aqueous solutions at 20 C. (pKa equals minus the logrithm of the equilibrium dissociation constant; pKa = log[1/Ka].)

2.4.1 Pyrroles (B.P. 130 C)

Pyrrole has an aromatic structure, is a reative compound, and is a weak base.(67,68) The alkyl-substituted pyrroles have greater basic strength, and, in some cases, relatively stable salts with hydrochloric acid have been obtained (e.g., 3-ethyl-2,4 dimethyl pyrrole has a pKa of 2.84). The weakly basic properties of pyrrole are masked by the fact that it readily polymerizes under the influence of mineral acid. Pyrrole has acidic properties but is a weaker acid than phenol and reacts with potassium (but not sodium) to liberate hydrogen to form a salt.

The nitrogen atom in pyrrole (unlike that in ammonia) has no "lone pair" of electrons not involved in bond formation. Pyrrole can form a salt only at the expense of its aromatic character, a fact that explains not only its weakly basic nature, but also its tendency to resinify when treated with strong acids. Because of the localization tendency of the π-electrons, reagents may attack pyrrole at different positions. The infrared absorption spectra of pyrrole show two types of NH bonds.

2.4.2. Indole (B.P. 254 C)

Indole is a benzo derivative of pyrrole and has similar electronic structure.(67,68) It can be obtained by heating pyrroles in the presence of zinc salts. Like pyrrole, indole is an extremely weak base and a weak acid. The resonance energy is 47 to 54 kcal/mole. As in pyrrole, the carbon atoms acquire some negative charge (particularly at the 3 position). Indole can be synthesized by the cyclization of two carbon chains in o-aminophenyl compounds, and the amino derivative is prepared via the corresponding o-nitro compound.

The substitution of halogen and nitro or nitroso groups on the benzene ring of indole does not occur.

2.4.3. Carbazoles (B.P. 355 C)

Carbazole is similar to pyrrole(67,68), but has a greater resonance energy (74 to 91 kcal/mole). The hydrogenated carbazoles become more basic. Carbazole dissolves in sulfuric acid to give a colorless solution. In oxidation reactions of tetrahydrocarbazole, an indole-carboxylic acid is obtained, i.e., the saturated benzene ring is destroyed.

The oxidation (e.g., with sodium dichromate or silver oxide) of carbazole forms dicarbazyls (two carbazoles linked at the nitrogen). Oxidation with potassium permanganate at 100 C is slowest compared with that for bituminous coal, pyrene, and naphthacene.(68)

The catalytic hydrogenation of pure carbazole over nickel does not occur even at 260 C and 450 psi, whereas substituted carbazoles are readily reduced. The outer ring is saturated with hydrogen and then cracks, leaving an indole. The mechanism of hydrocracking is discussed in a separate volume in a section on the kinetics of hydrodenitrification (HDN) reactions. Contrasted with other nitrogen heterocycles such as acridine, indole, and phenylpyrrole, carbazole is much more resistant to catalytic hydrogenation, and the tendency for hydrogen addition decreases in that order.

2.4.4. Benzonitriles (B.P. 190 C)

The removal of nitrogen from nitriles involves the breakage of the C≡N bond.(69) The carbon-nitrogen triple bond is stronger than the carbon-carbon triple bond (212 kcal vs 200 kcal) and is much more polar. The nitriles (-CN) can be reduced to amines ($-CN_2NH_2$) under controlled conditions with lithium-aluminum hydride. An aldehyde is formed from nitriles with an imine lithium salt. Hydrolysis of nitriles yields amides.

2.4.5. Benzamide (B.P. 290 C)

The amide ($-CONH_2$) group is reasonably polar and the lower-molecular weight amides are high melting and water soluble.(69) Amides with N-H bonds are weakly acidic but much more acidic than ammonia. Many cyclic amides undergo the Hofmann degradation (treatment with alkali). The unsubstituted amides are easily converted to carboxylic acids by treatment with nitrous acid; however, the disubstituted amides do not react.

2.4.6. Phenazine (B.P. >360 C)

This heterocyclic system is analogous to anthracene. Phenazine is a weak base (pKa 1.2), which is relatively resistant to electrophilic substitution. Nevertheless, it can be chlorinated and sulfonated provided the conditions are sufficiently rigorous. Monosulfonation, for example, can be effected with oleum and mercuric sulfate at 160 to 170 C. The major product is 2-phenazine sulfonic acid.

Oxidation with hydrogen peroxide gives phenazine-5,10-dioxide.

Reduction with lithium aluminum hydride gives 5-10-dihydrophenazine which in turn can be oxidized to phenazine.

2.4.7. Acridine (B.P. 345-346 C)

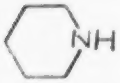
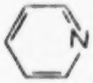
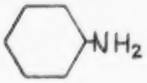
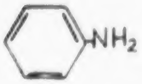
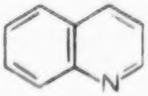
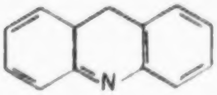
Acridine and its derivatives are highly conjugated and chemically stable aromatic compounds.(68) Acridine is a base with about the same strength as pyridine and aniline (pKa of 5.6). Its strength is lowered by electron-attracting substituents. Amino groups in the 2 or 5 position make acridine as basic as aliphatic amines. It remains unchanged after heating to 280 C with concentrated HCl or KOH. Hydrogenation is possible with Raney nickel to form acridan, but with sodium amalgum, a diacridyl is formed and formation of polyacridines is also possible. The best method of oxidation is to heat the acridine with sulfur in a sealed tube at 190 C and treat the thioacridone with sodium hypochlorite. A certain amount of addition occurs at the middle ring, e.g., halogen atom. Acridine hydrochlorite, nitrate, acid sulfate, dichromate, mercuric chloride, and picrate can be prepared. The properties of substituted acridines do not differ from those of acridine.

2.4.8. Amines

The physical properties of aliphatic and ring aromatic amines that occur in fuels are given in Table 33. The properties of amines depend on the degree of substitution on the nitrogen. Tertiary amines have no N-H bonds. Hydrogen bonding is weaker in amines than in alcohol systems. Amines can act as bases by accepting protons and the primary and secondary amines can act like weak acids as well. Complexes are formed with trimethyl boron, boron trichloride, and similar compounds.

Hydrogenolysis of pyridine is possible using hydrogen and a catalyst at high temperatures or with hydriodic acid. Electrophilic reagents attack pyridine with difficulty and are thus not attached in Friedel-Crafts reaction.

TABLE 33. PHYSICAL PROPERTIES OF SOME AMINES FOUND IN FUELS

Amine	Name	B.P., C	M.P., C	Water Solubility, g/100 ml
NH_3	Ammonia	-33	-77.7	90
CH_3NH_2	Methylamine	-6.5	-92.5	1156
$CH_3CH_2NH_2$	Ethylamine	16.6	-80.6	
$(CH_3)_3CNH_2$	t-butylamine	46	-67.5	
$(CH_3CH_2)_2NH$	Diethylamine	55.5	-50	v. sol.
$(CH_3CH_2)_3N$	Triethylamine	89.5	-115	1.5
$(CH_3CH_2CH_2CH_2)_3N$	Tri-n-butylamine	214		sl. sol.
	Piperidine	106	-9	
	Pyridine	115	-42	
	Cyclohexylamine	134		sl. sol.
	Aniline	184.4	-6.2	3.4
$H_2NCH_2CH_2NH_2$	Ethylenediamine	116	8.5	sol.
	Quinoline	237.7	-19.5	6
	Acridine	346	108	v. sl. s.

In halogenation, substitution occurs on the ring. Peracids are able to oxidize pyridine forming pyridine-N-oxide (-N-O) which can act as electron attracting or electron-donating group. Mercuration of the pyridine-N-oxide is possible.

Quinoline is stable and is used as a high boiling solvent. It is oxidized by potassium permanganate to give pyridine dicarboxylic acid, i.e., the ring in the quinoline not containing nitrogen is destroyed. Hydrogenation first saturates the nitrogen containing ring. Saturation of the nitrogen containing ring has been determined as a fast step compared to the ring cracking and ammonia evolution.

Acridine has a very stable ring system. The middle ring hydrogenates readily. With sodium hypochlorite oxidation leads to acridone.

In general the ring amines are more stable with respect to ring breakage and removal of nitrogen than aliphatic amines.

2.5 Characteristics of Trace-Element Contaminants in Coal/Coal Liquids

Volatile materials and fine particulate matter emitted into the atmosphere, or the disposal of such matter isolated in emission control systems, during coal combustion are considered potential environmental hazards. Major chemical constituents retained in fly ash, bottom ash, or other coal combustion residues may constitute long-term disposal hazards, particularly if they become soluble and enter groundwater or surface waters. With the advent of new analytical techniques, significant gains have been made in the knowledge relating to elements, other than C, H, S, N, and O, present in coal only in minor and trace amounts. Some of these trace elements in coal are known to be toxic to plant and animal life at relatively low concentrations and are potential pollutants. The concern over trace elements in coal has gone beyond their potential for environmental effects with development of large-scale coal-conversion operations. Certain trace elements, which may not even be classified as toxic, shorten the life of catalysts (catalyst poisons) used in liquefaction and gasification processes which are important in coal-derived fuel manufacture.

Minor and trace elements in coal as well as in coal that has undergone chemical modification to become coal liquids have their origin in the plant systems that made up the coal seams, the water and soils that isolated and surrounded the seams, the groundwater that flowed through the seams, and adjacent mineral beds during and after maturation of the coal. The final state of these elements was influenced by the chemical reactions that took place during maturation processes that converted the organic matter to the various coal ranks (lignite to anthracite). The residues from syngenetic processes of plants and the residues of microbial life left during transformation of plants to coal (which accounted for the part of the nitrogen and sulfur impurities in coal) also contributed to the retention of trace elements and the nature of their occurrence in the matured coals.

Identification of the minor elements and their quantitative determination in coal ash have been done for years. The composition of coal ash has been the subject of reviews.(70,71) Trace-element analyses of high-temperature (450 to 500 C) ash from thousands of coals have been reported.(72-76)

Such determinations provide a measure of the oxides of these elements that are retained by the ash because of their refractory characteristics, low volatility, or the chemical compounds formed during ashing. However, such determinations did not account for the trace elements in the raw, whole coal that are volatile at the high ashing temperatures. Recent advances in low-temperature ashing procedures and in the analysis of whole coal by neutron-activation analysis have been employed to overcome these shortcomings.

The utility of the low-temperature ashing technique as described by Gluskoter,(77) O'Gorman and Walker,(78) and Ruch et al(79,80) lies in the fact that coal and coal-like materials can be removed from a sample without grossly altering the mineral-matter composition as it existed in the raw coal. Analyses of such a low-temperature ash by X-ray diffraction and scanning electron microscopy have enabled the identification of unaltered mineral phases in coal and thereby the characterization of the occurrence of part of the trace elements in coal. Such mineral phases in coal have been postulated for many years and have been grouped into (a) epigenetic substances, or those added during coal formation, and (b) syngenetic substances, or those originating from the swamp biomass. Another system used more frequently by workers in coal research for differentiating the noncombustible components in coal is to characterize the mineral matter as either "inherent" or "extrinsic, extraneous, or adventitious".(78,81) Inherent mineral matter usually is defined as that portion of mineral matter originally combined with coal. It cannot be detected petrographically or separated by physical methods. This form of "mineral matter" consists of elements assimilated by growing plants, e.g., Si, Na, Mn, and Al or those essential to proper plant growth which Sprunk and O'Donnel(82) reported to be the elements Fe, P, S, Ca, K, and Mg. Extrinsic or adventitious mineral matter is readily detected petrographically and readily separated from coal. It may have originated during coal formation (syngenetic) or after the coal had formed (epigenetic).(78)

Analysis of whole coal by means of neutron-activation analysis (NAA) has provided the means by which trace and minor elements can be detected and quantitatively determined as they exist in whole coal. It provides a means of analysis for elements normally lost during high- and low-temperature ashing and those difficult to determine by other techniques (e.g., Hg, Sb, Se, As, Ga, Mn, Na).(79,80)

In coal utilization, exclusion of mineral matter in coal, including the trace elements, is desirable. In combustion, gasification, liquefaction, or carbonization processes, reduction of these materials to a minimum by proper coal cleaning and beneficiation is also desirable and perhaps even essential. Utilization of the wastes from cleaning operations and improving the separation procedures both require thorough understanding of the characteristics of minerals in coal and their role in coal and coal utilization. Part of this knowledge already exists in the vast number of experiments documented in the literature. The existing knowledge can be summarized by saying that mineral matter in coal is not uniformly distributed within a coal seam, but occurs as extensive layers of grains and rock fragments and as localized, thin, lenslike layers, grains, and rock fragments. Other noncombustible material classed as mineral matter occurs such that it is almost an integral part of the organic substance of coal itself. In this form, the elements normally are not released until coal structure itself is altered or destroyed.(81)

In processes using coal, the ultimate behavior of the coal is dependent to some extent on the amount and character of the noncombustible material present at the time the coal enters the process. In coal combustion, it influences the extent of boiler tube fouling and the fly-ash particle size distribution. In coal-conversion processes, ash-forming minerals have exhibited catalytic activity for gasification and liquefaction. Therefore, knowledge of the amount and character of the mineral matter or noncombustible portion of coal can provide a basis for intelligent selection of a coal for utilization in a particular process. Control and/or removal of trace elements is essential to limiting the pollution inherent to these trace elements in large-scale coal-utilization operations. Detailed characterization of these trace elements should provide a better understanding of the development of control methods and the possible limits of existing control methods.

2.5.1. Trace Elements Identified in Coal

Of 73 elements of the periodic table analyzed for in 13 raw (whole) coal, 44 elements were found in all the coals, 12 elements were found in >75 percent of the coals, 8 elements were found in about 50 percent of the coals, and 9 elements were sought but not detected in any of the coals. The concentrations ranged from 0.01 to 41,000 ppm.(83) The results of spark-source mass spectrometric analysis of 13 coals are summarized in Figures 8 and 9. Figure 8 shows the frequency of occurrence in these 13 coals. Figure 9 shows the ranges of the concentrations found in these same coals. This information, in the periodic-table format, was taken from Sharkey, et al.(83)

Black and Dams(84) using neutron-activation analyses on whole coal reported on 43 elements in coal. Emission spectroscopy has been used primarily on ash from coal samples to identify the 36 elements. Most work on determination of trace elements in whole coal is fairly recent. The accuracy of the analytical techniques, especially those newly developed, has been open to question because of the lack of standards and lack of knowledge of the range of concentrations for many trace elements in coal. Methods of analysis of an NBS-EPA round-robin coal sample have been evaluated by various laboratories. These programs were aimed at developing coal standards through the means of the round-robin program. The 43 elements and their mean concentration (in ppm) in the round-robin coal sample, determined by NAA at the Lewis Research Center of the NASA, are given in Table 34.(85) Another set of determinations by NAA, done at Battelle's Pacific Northwest Laboratories, are presented in Table 35 for comparison.(86) Only four of the participating laboratories reported mercury, and in all but one, the values on the whole coal were greater than those on the samples analyzed by destructive methods.

H ND																
Li 100	Be 100											B 100	C ND	N ND	O ND	F 100
Na 100	Mg 100											Al 100	Si 100	P 100	S 100	Cl 100
K 100	Ca 100	Sc 100	Ti 100	V 100	Cr 100	Mn 100	Fe 100	Co 100	Ni 100	Cu 100	Zn 100	Ga 100	Ge 100	As 100	Se 100	Br 100
Rb 100	Sr 100	Y 100	Zr 100	Nb 100	Mo 100	Tc Nd	Ru 0	Rh 0	Pd 0	Ag 92	Cd 92	In Standard	Sn 100	Sb 92	Te 85	I 85
Cs 100	Ba 100	La 100	Hf 46	Ta 62	W 69	Re 0	Os 0	Ir 0	Pt 0	Au 0	Hg 38	Tl 31	Pb 100	Bi 31	Po ND	At ND
Fr ND	Ra ND	Ac ND	Ce 100	Pr 100	Nd 100	Pm ND	Sm 100	Eu 100	Gd 85	Tb 85	Dy 85	Ho 77	Er 77	Tm 0	Yb 62	Lu 38
			Th 92	Pa ND	U 92											

FIGURE 8. OCCURRENCE FREQUENCY OF ELEMENTS IN 13 RAW COALS AS DETERMINED BY SPARK-SOURCE MASS SPECTROMETRY. ALL QUANTITIES IN PERCENT. ND = NOT DETERMINED. 0 = CHECKED BUT NOT DETECTED.(83)

H ND																
Li 4-163	Be 0.4-3											B 1-230	C ND	N ND	O ND	F 1-110
Na 100-1,000	Mg 500-3,500											Al 3,000-23,000	Si 5,000-41,000	P 6-310	S 700-10,000	Cl 10-1500
K 300-6,500	Ca 800-6,100	Sc 3-30	Ti 200-1,800	V 2-77	Cr 26-400	Mn 5-240	Fe 1400-12,000	Co 1-90	Ni 3-60	Cu 3-180	Zn 3-80	Ga 0.3-10	Ge 0.03-1	As 1-10	Se 0.04-0.3	Br 1-23
Rb 1-150	Sr 17-1,000	Y 3-25	Zr 28-300	Nb 5-41	Mo 1-5	Tc ND	Ru <0.1	Rh <0.1	Pd <0.1	Ag <0.01-3	Cd <0.01-0.7	In Standard	Sn 1-47	Sb <0.1-2	Te <0.1-0.4	I <0.1-4
Cs 0.2-9	Ba 20-1,600	La 0.3-29	Hf <0.3-4	Ta <0.1-8	W <0.1-0.4	Re <0.2	Os <0.2	Ir <0.2	Pt <0.3	Au <0.1	Hg <0.3-0.5	Tl <0.1-0.3	Pb 1-38	Bi <0.1-0.2	Po ND	At ND
Fr ND	Ra ND	Ac ND	Ce 1-30	Pr 1-8	Nd 4-36	Pm ND	Sm 1-6	Eu <0.1-0.4	Gd <0.1-3	Tb <0.1-2	Dy <0.1-5	Ho <0.1-0.4	Er <0.1-0.4	Tm <0.1	Yb <0.1-0.5	Lu <0.1-0.3
			Th <0.1-5	Pa ND	U <0.1-1											

FIGURE 9. CONCENTRATION RANGE OF ELEMENTS IN 13 RAW COALS ANALYZED BY SPARK-SOURCE MASS SPECTROMETRY. ALL QUANTITIES IN PPM WEIGHT. ND = NOT DETERMINED.(83)

TABLE 34. PRECISION ON NBS-EPA ROUND-ROBIN COAL SAMPLE(a)(85)

Element	Mean, ppm	± 1σ, ppm	Standard Deviation, percent
Al	15,700	1,550	9
As	5.9	0.5	9
Au	0.146	0.048	33
Br	20	3	15
Ba	337	42	12
Ca	4,070	560	14
Ce	17.340	0.089	2
Cl	750	75	10
Co	5.48	0.15	3
Cr	19	0.8	4
Cs	2.55	0.06	2.3
Cu	14.1	0.9	6
Dy	0.85	0.06	7
Eu	0.312	0.037	12
Fe	7,517	119	2
Ga	5.4	0.8	14
Ge	70	5	7
Hf	0.92	0.05	6
Hg	0.95	0.09	10
I	2.78	0.38	14
In	0.04	0.01	25
Ir	2.48	0.27	11
K	3,500	360	10
La	11.3	3.3	30
Lu	0.416	0.017	4
Mg	980	250	26
Mn	38.0	2.6	7
Na	370	33	9
Nd	6.4	1.5	24
Rb	19	1.9	10
Sb	6.4	1.6	24
Se	3.8	0.51	13
Sm	1.3	0.19	15
Sn	125	20	16
Sr	93	9.2	10
Ta	0.360	0.028	8
Tb	0.03	0	0
Th	3.1	0.2	8
Ti	1,312	150	12
U	0.980	0.078	8
V	36	4	11
W	1.9	0.8	40
Yb	0.55	0.04	8

(a) Analysis performed by NASA Lewis Research Center.

TABLE 35. ELEMENTAL COMPOSITION OF(86)
NBS-EPA COAL STANDARDS
(PPM Except as Noted)(a)

Element	Coal*
Al (percent)	1.78 ± 0.08
Ag	0.06 ± 0.03
As	5.7 ± 0.5
Au	< 0.03
Ba (percent)	0.039 ± 0.002
Br	17 ± 2
Cd	< 2.1
Cl (percent)	0.08 ± 0.02
Co	5.2 ± 0.4
Cr	19 ± 2
Cs	1.4 ± 0.1
Cu (percent)	< 0.007
Eu	0.28 ± 0.01
Fe (percent)	0.81 ± 0.07
Hf	0.97 ± 0.10
Hg	--
K (percent)	0.28 ± 0.01 (0.284 ± 0.008)
La	10.5 ± 0.5
Mg (percent)	0.23 ± 0.07
Mn	41 ± 6
Na (percent)	0.042 ± 0.003
Ni	16 ± 4
Rb	19 ± 2
Sb	3.7 ± 2.0
Sc	3.4 ± 0.3
Se	3.3 ± 0.4
Sm	1.7 ± 0.3
Sr (percent)	0.017 ± 0.001
Ta	0.46 ± 0.05
Tb	0.23 ± 0.06
Th	3.4 ± 0.6 (3.45 ± 0.10)
Ti (percent)	0.11 ± 0.02
U	(1.41 ± 0.07)
V	33 ± 4
Yb	--

* Average and standard deviation of 6 determinations.

( ) - Number from Na I (Tl) multidimensional γ-ray spectrometry.

(a) Analysis performed by Battelle Pacific Northwest Laboratories.

Extensive data on the amount of trace elements in coal and on their mode of occurrence have been published by the staff at Illinois State Geological Survey (ISGS).(79,80) The authors reviewed work on coal trace-element characterization and provided new information on the trace elements in 101 coals, especially as it related to whole coal analysis. The study has shown that when high-temperature ashing techniques are used in sample preparation, part of the trace elements are volatilized. Some trace elements are lost even with low-temperature ashing. In particular, the study showed that the elements Hg, Br, F, and Sb are volatilized at 150 C (Hg ~ 90 percent, Br ~ 100 percent, Sb ~ 50 per cent, F presumed 100 percent), while Ga, Se, and As are volatilized at 450 to 500 C. Molybdenum and vanadium are partially lost during 450 to 500 C ashing. Therefore, only the most recent values from whole-coal analysis or from the analyses of low-temperature plasma ash would appear to be providing an accurate measure of all the trace elements reported on in whole coal. The residues from low-temperature ashing also provide the best form in which to identify mineral matter in coal.

The mean analytical values of elements for which determinations were made in the 101 coals are given in Table 36. A statistical analysis of the large amount of data generated from the analytical results for 101 whole-coal samples provided some important general relationships.(80) These are:

- A near normal distribution of analytical values with small standard deviations and ranges was found for the elements Al, Fe, F, Ga, Br, B, Cr, Cu, K, Ni, Si, Ti, Se, and V (always present).
- Of the group of elements consisting of Cd, Zn, P, As, Sb, Pb, Sn, Cl, Ge, and Hg, each exhibited a highly skewed distribution with large standard deviations and ranges (presence varies).
- Positive correlation coefficients existed for Zn and Cd, for the group As, Co, Cu, Ni, Pb, and Sb (known chalcophiles), for the group Si, Al, Ti, and K (known lithophiles), for Mn and Ca (known carbonates), and for Na and Cl (brines).

TABLE 36. MEAN ANALYTICAL VALUES FOR 101 COALS (80)

Constituent	Mean	Unit	STD	MIN	MAX
As	14.02	PPM	17.70	0.50	93.00
B	102.21	PPM	54.65	5.00	224.00
Be	1.61	PPM	0.82	0.20	4.00
Br	15.42	PPM	5.92	4.00	52.00
Cd	2.52	PPM	7.60	0.10	65.00
Co	9.57	PPM	7.26	1.00	43.00
Cr	13.75	PPM	7.26	4.00	54.00
Cu	15.16	PPM	8.12	5.00	61.00
F	60.94	PPM	20.99	25.00	143.00
Ga	3.12	PPM	1.06	1.10	7.50
Ge	6.59	PPM	6.71	1.00	43.00
Hg	0.20	PPM	0.20	0.02	1.60
Mn	49.40	PPM	40.15	6.00	181.00
Mo	7.54	PPM	5.96	1.00	30.00
Ni	21.07	PPM	12.35	3.00	80.00
P	71.10	PPM	72.81	5.00	400.00
Pb	34.78	PPM	43.69	4.00	218.00
Sb	1.26	PPM	1.32	0.20	8.90
Se	2.08	PPM	1.10	0.45	7.70
Sn	4.79	PPM	6.15	1.00	51.00
V	32.71	PPM	12.03	11.00	78.00
Zn	272.29	PPM	694.23	6.00	5350.00
Zr	72.46	PPM	57.76	8.00	133.00
Al	1.29	Percent	0.45	0.43	3.04
Ca	0.77	Percent	0.55	0.05	2.67
Cl	0.14	Percent	0.14	0.01	0.54
Fe	1.92	Percent	0.79	0.34	4.32
K	0.16	Percent	0.06	0.02	0.43
Mg	0.05	Percent	0.04	0.01	0.25
Na	0.05	Percent	0.04	0.00	0.20
Si	2.49	Percent	0.80	0.58	6.09
Ti	0.07	Percent	0.02	0.02	0.15
ORS	1.41	Percent	0.65	0.31	3.09
PYS	1.76	Percent	0.86	0.06	3.78
SUS	0.10	Percent	0.19	0.01	1.06
TOS	3.27	Percent	1.35	0.42	6.47
SXRF	2.91	Percent	1.24	0.54	5.40
ADL	7.70	Percent	3.47	1.40	16.70
MOIS	9.05	Percent	5.05	0.01	20.70
VOL	39.70	Percent	4.27	18.90	52.70
FIXC	48.82	Percent	4.95	34.60	65.40
ASH	11.44	Percent	2.89	2.20	25.80
BTU/LB	12748.91		465.50	11562.50	14362.00
C	70.28	Percent	3.87	55.23	80.14
H	4.95	Percent	0.31	4.03	5.79
N	1.30	Percent	0.22	0.78	1.84
O	8.68	Percent	2.44	4.15	16.03
HTA	11.41	Percent	2.95	3.28	25.85
LTA	15.28	Percent	4.04	3.82	31.70

Note: Abbreviations other than standard chemical symbols: organic sulfur (ORS), pyritic sulfur (PYS), sulfate sulfur (SUS), total sulfur (TOS), sulfur by X-ray fluorescence (SXRF), air-dry loss (ADL), moisture (MOIS), volatile matter (VOL), fixed carbon (FIXC), high-temperature ash (HTA), low-temperature ash (LTA).

- Only the elements Cd, B, and Se were found to be enriched in coal to values greater than the average composition of the earth's crust. The elements F, Mn, and P were found to be depleted to values below the average composition of the earth's crust.

The last relationship, which reflects refinements in analytical procedures, is considerably different from that presented by earlier workers whose comparisons of values with those of the earth's crust were made from coal-ash analyses (Reference 80 for example).

Extensive work has been reported on the variation of trace elements in columns of coal taken from the full height of the seams throughout the United States. To compile such information and present a generalized characterization of all coals would be difficult. However, some of the generalizations made on the occurrence of the trace elements in large numbers of coal seams provides additional bases for understanding the nature of their occurrence in coal. A typically thorough study is the work done on the distribution of 35 elements in West Virginia coals.(80) A summary on the mechanism of retention and the occurrence of trace elements is given in Table 37. (Secondary mineralization implies chemical changes that occurred after the organic mass of the coal bed was in place.)

The analysis of coal fractions separated by specific gravity differences (i.e., washed coals or float-sink fractions separated by means of specific gravity differences) provides information on the distribution of trace elements in coal more relevant to establishing their occurrence and to their potential for removal from coal. A correlation of the trace-element concentrations in such fractions has been reported.(79,80) From the analyses of 8 fractions from 4 coals, the trace elements were classified into four groups as follow:

1. The elements in the first group, Ge, Be, and B, have the greatest affinity for the organic phase and tend to be concentrated in the coal fractions isolated in the lower specific-gravity range (1.28 to 1.31), i.e., the clean coal fractions.

TABLE 37. DISTRIBUTION OF TRACE ELEMENTS IN COAL SEAMS AND PROBABLE MODE OF MINERALIZATION(81)

Element	Distribution or Mode of Mineralization
As	Distribution in coal seam suggests that arsenic is not concentrated by secondary mineralization.
B	Distribution in coal seam suggests secondary mineralization process for its presence; trend is reverse of germanuim and antimony concentration.
Be	Present in low- and high-ash coals, indicating origin from secondary mineralization processes; highest values at top and bottom of seams.
Bi	No evidence for secondary mineralization; associated with high-ash coals.
Co	Secondary mineralization may or may not be the cause of high-cobalt regions.
Cr	No evidence for secondary mineralization; uniformly distributed between coals and shales near bottom of seam.
Cu	Distributions are uniform; in low-ash coals, random higher values are due to secondary mineralization.
Ga	High values appear in low-ash coals, usually in top and bottom of coal seam.
Ge	Appears to be in the organic matter rather than associated with mineral matter; absorbed by the coal from water carrying germanuim salts in solution and most concentrated in top and bottom of seam.
Hg	No evidence for secondary mineralization.
Mn	Wide range of distribution due to secondary mineralization.
Mo	Random distribution due to secondary mineralization.
Ni	Variable distribution in coal seam suggesting some secondary mineralization.
P	High phosphorous values occur in regular intervals and independent of ash content. (Exclusion of such intervals during mining would produce low-phosphorus coal for metallurgical purposes.)
Pb	Distribution varies with region and suggests secondary mineralization.
Sb	Similar to Ge; highest concentration at top and bottom of seam.
Sn	Most high values are in coals with low ash < 3 percent; high tin associated with low inherent ash; secondary mineralization suggested by distribution in coal seams.
V	Distribution random but quite uniform; shales have the same concentrations as coal ashes.
Zn	Shale and ash have similar values and the maximum is just slightly greater than median concentation, suggesting that no secondary mineralization occurs.
Zr	Has uniform symetrical distribution in coal seam.

2. The elements in the second group are those with the least organic affinity and are found concentrated in the mineral matter in coal. The elements in this group are Hg, Zr, Zn, Cd, As, Pb, Mn, and Mo.
3. The elements in the third group, P, Ga, Ti, Sb, and V, are assumed to be associated with both organic and inorganic materials in coal but are more closely tied to the elements with the highest organic affinity, i.e., Ge, Be, and B.
4. The elements in the fourth group, Co, Ni, Cr, Se, and Cu, were also found to be associated with organic and inorganic materials in coal. However, they are more closely tied to the elements known to be inorganically related, i.e., Group 2 above.

These correlations are summarized in Table 38.

Development of correlations of the occurrence of trace metals with the organic phase of coals as determined in five different density fractions has been a subject of a review by Zubovic.(87) The results of such a correlation in which the distribution of the elements with organic and inorganic matter were ranked are given in Table 39. There is general agreement between trends reported in the table and those summarized in more recent work (Table 40).(80,88) Similar studies on lignites have shown that Na, Ca, and Mg, although minor elements rather than trace elements, report to the float fraction (sp gr < 1.59), while Fe, S, Si, Al, and Cu report to the sink fraction.(89) The distribution of these metals in fractions with other specific gravities was not reported in this study.

2.5.2. Trace Elements Associated With Mineral Matter in Coal

The meaning of the term mineral matter in coal has generally been accepted to include all inorganic, noncoal material present in coal as mineral phases and all elements in coal that are considered inorganic (i.e.,

TABLE 38. CORRELATION OF TRACE ELEMENT DISTRIBUTION IN WASHED COAL FRACTIONS(80)

Clean Coal Organic Matrix	Decrease in Organic Content →		Mineral Matter Inorganic Matrix
Coals Only ⟷	Clays and Coal Combination ⟷	Partly as Sulfides ⟷	Sulfides and Carbonates
Ge(a) Be(a) B(a)	P(b) Ga Ti(b) V Sb	Co Ni Cr Se(b) Cu(b)	Hg Zn Zr Cd (Sulfides) As Pb Mo Mn (Carbonates)
	Fractions from Wash Media of Specific Gravity		
1.29	1.31 1.40	1.60 2.89	> 2.9

(a) Mostly in organic phase but also present in heavier inorganic fractions.

(b) Mostly in inorganic phase but also present in organic.

TABLE 39. AVERAGE ORGANIC AFFINITY OF SOME METALS DETERMINED BY FLOAT-SINK METHODS(87)

Element	Percent Organic Affinity(18)	Percent Organic Association(21)
Germanium	87	100
Beryllium	82	75-100
Gallium	79	75-100
Titanium	78	75-100
Boron	77	75-100
Vanadium	76	100
Nickel	59	0-75
Chromium	55	0-100
Cobalt	53	25-50
Yttrium	53	N.D.(a)
Molybdenum	40	50-75
Copper	34	25-50
Tin	27	0
Lanthanum	3	N.D.(a)
Zinc	0	50

(a) N.D. - not determined.

TABLE 40. AFFINITY OF ELEMENTS FOR PURE COAL AND MINERAL MATTER AS DETERMINED FROM FLOAT-SINK DATA(88)

	Davis Coal	DeKoven Coal	Colchester (No. 2) Coal	Herrin (No. 6) Coal
Clean coal - lightest specific gravity fraction (elements in "organic combination")	B	Ge	Ge	Ge
	Ge	Ga	B	B
	Be	Be	P	Be
↕	Ti	Ti	Be	Sb
	Ga	Sb	Sb	V
	P	Co	Ti	Mo
	V	P	Co	Ga
	Cr	Ni	Se	P
	Sb	Cu	Ga	Se
	Se	Se	V	Ni
	Co	Cr	Ni	Cr
	Cu	Mn	Pb	Co
	Ni	Zn	Cu	Cu
	Mn	Zr	Hg	Ti
	Zr	V	Zr	Zr
	Mo	Mo	Cr	Pb
	Cd	Pb	Mn	Mn
Mineral matter - specific gravity greater than 1.60 (elements in "inorganic combination")	Hg	Hg	As	As
	Pb	As	Mo	Cd
	Zn		Cd	Zn
	As		Zn	Hg

other than C, H, N, O, S). Of course, carbon is also found as carbonates; hydrogen as water of hydration or crystallization; oxygen as oxides, sulfates, and silicates in addition to those above; and sulfur as sulfides or as sulfate.(78-80)

Analysis of a very large number of coals for their mineral-matter content has given a range of 9.05 to 32.26 percent mineral matter in coal with 15 percent being a reasonable estimate of the average value for coals in North America.(70)

The total mineral matter contained in whole coal has, until recently, been a value estimated from the coal-ash analysis and various formulas.(70,77,78) More recently, with development of low-temperature ashing techniques, precise mineral-content determinations for coal have been made.(77-80) This has permitted calculation of mineral-to-ash ratios for a large number of coals. The average ratio is about 1.10, with a range of values from 0.97 to 1.32. About 80 percent of the ratios fall between 1.02 and 1.17 for the coals studied.(77,80) Ratios less than unity are possible if the mineral matter gained weight during ashing, e.g., oxide going to carbonate or sulfide to sulfate. The assumption made in the development of this ratio was that the values obtained after low-temperature ashing were identical with the mineral matter in coal. Except for a few elements that volatilize during low-temperature ashing, this is about as close as researchers have been able to come to an absolute mineral-matter determination.

The importance of the characterization of mineral matter in coal and its constituents is to provide a more thorough knowledge of their concentrations, distribution in coals, their volatility, and their potential effects on the environment during combustion or coal conversion. Their role in the conversion of coal to gases, liquids, and clean fuels has become increasingly important and greater knowledge of their characteristics should aid in solving the problems of their removal and disposal.

A recent review on the subject of mineral matter and trace elements in coal categorized the major minerals in coal into four groups.(88)

1. Aluminosilicates - Clay Minerals. Most commonly occurring minerals are illite [$K_2(Si_6 \cdot Al_2)(OH)_4Al_4O_{20}$], kaolinite [$Si_4Al_4O_{10}(OH)_8$], and an illite-montmorillonite

mixture. Their amount in coal varies but a mean value of 52 percent of the mineral matter in coal has been reported for Illinois coals.(90) Other investigations have obtained similar results for other U.S. coals.(78)

2. Sulfides and Sulfates. Pyrite and its dimorph, marcasite, are the major sulfides (FeS_2). Other sulfides identified are sphalerite (ZnS) and galena (PbS). Sulfates are not common and often are not present in fresh unweathered coal. The salts are the various hydrates of ferrous sulfate and ferric-ferrous sulfate mixtures. In Illinois coals, the sulfides and sulfates make up about 25 percent of the mineral-matter content.(90) In low-sulfur coals, the contribution of the sulfide minerals to the total mineral matter is much less since only a small amount of the total sulfur present is due to pyritic sulfur.
3. Carbonates. Carbonate minerals, because of the potential for solid-solution formation of calcium, magnesium, iron, and manganese, vary in composition. Pure calcite ($CaCO_3$) and siderite ($FeCO_3$) have been reported. The most frequent minerals are dolomite ($CaCO_3 \cdot MgCO_3$) and ankerite ($2CaCO_3 \cdot MgCO_3 \cdot FeCO_3$). Carbonate minerals make up 9 percent of Illinois coals.(90) The mineral phase varies with regions.
4. Silica (Quartz). Illinois coals average about 15 percent silica. Values of 1 to 20 percent have been found in other U.S. coals.(78)

In addition to the minerals cited above, apatite has been definitely isolated and identified [$Ca_5(PO_4)_3(FCO_3)$].

Older categorizations covered in reviews are not appreciably different (see Table 41).(70) Analyses of coals from numerous worldwide regions have identified minerals from the identical groups. Studies on lignite residues in which low-temperature ashing was employed have indicated that nitrates of sodium and the alkaline earth were present.(78,91) (There is some question as to whether or not the nitrate may have been formed from oxygen and nitrogen gas dissociates during low-temperature ashing in the highly energetic radio frequency plasma.) Other studies with lignites from the northern great plains coal provinces have shown that the minerals nacrite [$Al_2Si_2O_5(OH)_4$] and barite ($BaSO_4$) are also present in coals.(89) It is the general conclusion that the major types of mineral matter present in coal are kaolinite, illite-montmorillinite, and quartz.(70,78,88) For high-sulfur coals, pyrites are included in the list.(88)

As in all mineral systems, the substitution in the mineral lattice of one element for another occurs frequently and is not unexpected. This is especially true when metals with the same oxidation state (ionic charge) or similar size (ionic radii) are involved. Therefore, positive correlations of various trace elements with the host mineral elements is not unexpected. Such a correlation was developed for the minerals identified in a recent study.(79,80) The results are given in Table 42, which shows the mineral phase and the principal elements of which it is composed. Opposite each mineral listed in Table 42 are the elements found to have a positive correlation with this mineral phase. Those elements in parentheses in the right-hand column were not detected as such in the mineral.

Physical Characteristics of Mineral Matter in Coal. O'Gorman and Walker in their studies on the amounts of major minerals present in four coals of different rank found wide differences in mineral-matter composition.(78) Physical characterization of the products from low-temperature ashing were performed and this included surface area measurements by low-temperature absorption techniques and true density measurements. The surface area varied

TABLE 41. MINERALS ASSOCIATED WITH BRITISH BITUMINOUS COALS(70)

Group	Species	
Shales	Muscovite	Bravasite
	Hydromuscovite	Montmorillonite
	Illite	
Kaolins	Kaolinite	Metahalloysite
	Livesite	
Sulfides	Pyrite	Marcasite
Carbonates	Ankerite	Ankeritic dolomite
	Ankeritic calcite	Ankeritic chalybite
Chlorides	Sylvine	Halite
Accessory Minerals	Quartz	Prochlorite
	Feldspar	Diaspore
	Garnet	Lepidocrocite
	Hornblende	Magnetite
	Gypsum	Kyanite
	Apatite	Staurolite
	Zicron	Topaz
	Epidote	Tourmaline
	Biotite	Hermatite
	Augite	Penninite

TABLE 42. TRACE ELEMENT--COAL MINERAL SPECIES CORRELATIONS (80)

Mineral Group. Principal Elements	Element With Positive[a] Correlation With Mineral
Sphalerite, ZnS	Zn, Cd, (Hg, B)
Galena, PbS	Pb (Hg)
Apatite, $Ca_5(PO_4)_3(F,CO_3)$	Ca, P, F
Pyrite, FeS_2	Ni, Cu (As, Be, Sb)
Kaolinite, aluminosilicate	Si, Al, Ti, K, (B, Cu, F, Hg, Sn, V)
Quartz, SiO_2	(B, Cr, Mn, Cd, Mo, Se, V, Zn)
Calcite, $CaCO_3$	Mn (B, Cd, Mo, Se, V)

(a) Elements in parentheses in this column have not been detected in specific mineral phases; however, a positive correlation existed.

from 5.1 to 14.3 m^2/g and the densities varied from 2.79 to 3.39 g/cm^3. The densities agreed closely with those calculated from the mineral-matter compositions and known true densities of individual minerals. (Both of these physical characteristics will affect the ease of their separation from coal when physical methods are used.)

Handbook values of the specific gravities of the mineral phases identified by Ruch, et al (80) are given below:

Mineral	Specific Gravity Range
Sphalerite	3.90 - 4.11
Galena	7.3 - 7.6
Apatite	3.15 - 3.27
Pyrite	4.95 - 5.17
Kaolinite	2.60 - 2.63
Quartz	2.59 - 2.66
Calcite	2.71
Dolomite (Ankerite)	2.80 - 2.99
Siderite	3.0 - 3.88

The characteristic property of most clay and shale associated with coal is disintegration in water to smaller particle sizes. Such behavior affects washery-water clarification, dewatering, and drying of the fine sizes of coal, contamination and increased viscosity of dense-medium suspensions, filtration of froth-flotation-cleaned coal, and the refuse and the handling and disposal of fine refuse. Clay and shale swell in particle size to such an extent that the specific gravity is decreased from 2.1 for dry material to less than 1.60. When this happens, shale and clay may be discharged along with the washed coal.(92)

2.5.3. Trace Metals Associated With Organic Matter in Coal

The behavior of the elements Ge, Be, B, and sometimes Ti and U during coal cleaning or coal-conversion processes and the differences in the distribution of these trace elements in specific-gravity fractions of younger (lignites and brown coals) and older coals suggest that the nature of their occurrence in coal is tied more closely to the organic matter in coal and less with the mineral matter.

Germanium in Coal. Early reports on the distribution of germanium in coal have shown that bituminous coal fractions with a specific gravity of <1.31 contained most of the germanium.(93) In lignites, germanium could be found only in association with the mineral matter, even though both uranium and arsenic were found only in the organic matter.(94) (In this case the arsenic was assumed to have originated from the oxidation of arsenopyrite during aging and was captured by the organic matter as oxidized arsenic compounds.) Other lignites are reported to contain germanium, which during low-temperature charring exhibits little or no loss of the element during the process (as contrasted to the losses during combustion and concentration in the fly ash).(95) Germanium also could not be detected in coal washing refuse indicating low levels in mineral matter. Typically, higher germanium concentrations are found in low-ash coals, and the regions of maximum accumulation were in the vicinity of zinc and lead ore deposits.(96,97) Germanium is usually concentrated near the top and bottom of coal seams. These regions also have high concentrations of Be, Ca, Cr, and Ni. The same research group noted that the vitrinites (wood portion) contained absorbed water-soluble germanium and acid-soluble germanium combined with iron hydroxides and sulfides, and suggested that a considerable part of the germanium in coal was found in free inorganic matter, chiefly in the form of pyrites (Ge^{++} + Fe^{++} have similar ionic radii).(96) In contrast, workers in Russia have shown that germanium is bound in coal by functional groups in the coal structure and is partially in a relatively mobile form.(98) The mobile portion was extracted from known coals and lignites with complexing reagents such as pyrocatechol and tartaric acid (removed $\leq$ 35 percent of germanium present). This suggested that germanium was bound to the coal functional groups by ionic and coordination bonds. The more tightly bound germanium can be solubilized only by decomposition of the coal structure binding it.

The forms of binding of germanium in solid fuels have been the subject of a recent study which demonstrated, by selective reactivity with reagents, that three types of binding hold germanium in coal and that their proportions are related to the coal types being investigated.(99) Complex humate salts of germanium form O-Ge-O bonds which are readily hydrolyzed by strong acids such as hydrochloric acid. The germanium-organic compounds which have a Ge-C bond are resistant to acid treatment and require oxidation at 300 C before the acid treatment is effective in the removal of the germanium. The germanium untouched by either of these processes is that present as silica-germanates or a solid solution of GeO_2 in SiO_2. The proportion of these types of germanium compounds in solid fuels is given in Table 43.(99)

Titanium in Coal. Titanium is found in all coal seams, in concentrations varying from about 0.3 to 0.15 percent TiO_2 in coal ash. The concentration does not appear to be related to rank of the coal nor geographic location. The primary distinction of titanium in coal is its wide variability even though some removal can be accomplished by gravity separation.(97)

Uranium in Coal. There are sizable amounts of uranium in the low-rank coals of the western United States, and in certain locations its concertration approaches or exceeds ore-grade specifications for uranium. Lignites contain the highest concentrations. The fact that coals with the highest uranium levels do not show individual minerals of uranium (autunite, carnotite, etc.) suggest that it is held in the coal as an organo-uranium complex which is soluble (decomposes) at pH less than 2.18. Recovery from coal, however, usually is done after combustion, using acid leaching of the ash (lignite ash is alkaline in character due to the sodium and calcium associated with it).(97)

Chemistry of Metals Associated with Organic Matter. The affinity of some metals for the organic phase, determined on float-sink fractions, was summarized by Zubovic(87) and was presented earlier in Table 39. To explain these trends, Zubovic postulated that these metals are present in the most stable complex possible, i.e., as chelated metal-organic complexes forming 5- and 6-member rings with the metal. Metal ions with a

TABLE 43. FORMS OF BINDING OF GERMANIUM IN SOLID FUELS(99)

Type of Solid Fuel	Bound Germanium in Percent of Initial Sample		
	In the Form of Complex Humates	In the Form of Germanium-Organic Compounds	As Silicogermanates or Solid Solutions
Peat	21	16	63
Brown coal (lignite)	58	15	27
Brown coal (lignite)	90	none	10
High-volatile bituminous coal	18	none	82

high ratio of ionic charge to ion radius would be the preferred species undergoing complex formation. The stability of chelated complexes of bivalent metal ions prepared in the laboratory is on the order of Be>Cu>Ni>Co>Zn>Fe. For tervalent ions, the stability trend is Ga>Y>La. Strikingly, this is the same order of affinity (except for copper) for organics given in Table 39. Zubovic postulated, on the basis of this observed organic affinity and the stability of the complexes of these metals, that portions of the Ga, Y, La, Be, Ni, Co, and Zn bonded to organic matter in coal are held as chelated complexes. In the light of more recent data, even the metals Ge, B, Ti, and V, for which adequate experimental data could not be found by Zubovic to support the existence of complex formation, can now be included in the list. The relationships developed in this work are summarized in Figure 10. In Figure 10, the plot of the percentage of metal associated with organic material versus the order of decreasing affinity produces three sets of trend lines. A similar pattern, shown in Figure 10, is obtained when the affinity is plotted against the ratio of the ion charge to ion radii (ionic potential).

Ligand Effect. The nature of the donor atom in the organic molecule or ligand making the complex (O, N or S) plays an important role in stability of the complexes formed with metals. More stable complexes are formed when the metal bonds to preferred atoms. For example, complexes of Ga, Ge, Ti, Sn, V(IV), V(V), and Co all prefer oxygen to nitrogen. Complexes of Cu(II), Cu(I), V(III), and Ni(II) ions prefer nitrogen to oxygen. Ge, Cr, Fe, and Be form complexes of equal stability with either oxygen- or nitrogen-containing organic molecules.

Such considerations suggested to Zubovic(87) that complex-forming ligands present in decomposing plant remains which could form metal chelates could include chlorophyl (porphyrin), amino acids, and lignin derivatives. He postulated that V(III), Ni, Cu, and Fe would be chelated by the nitrogen donor atoms in porphyrin and the amino acids systems. The oxygen in lignin derivatives would form complexes with Be, Ge, Ga, Ti, Ca, Al, and Si.

In the former set, preservation of amino acids in carbonaceous materials could be related to very stable complex formations through chelation or ring formation with the metal atoms. The vanadium or nickel porphyrin complexes in petroleum have been well characterized (see section on trace

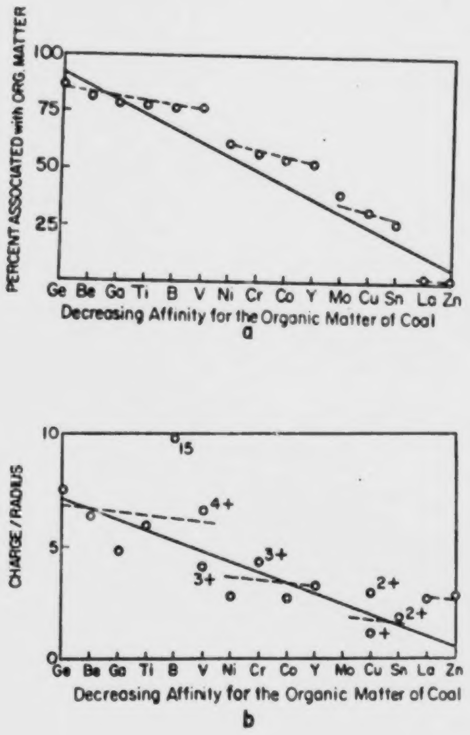
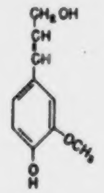


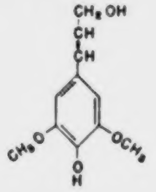
FIGURE 10. RELATION OF ORGANIC AFFINITY AND IONIC POTENTIAL OF THE ELEMENTS(87)

metals in petroleum) and the stability of these nitrogen chelate complexes explains their survival throughout maturation processes forming the fossil fuel.

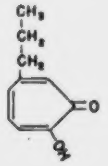
The oxygen in lignin derivatives such as those formed by depolymerization and degradation form complexes usually through carboxylic acid or phenolic functional groups. Some proposed systems are:



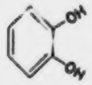
coniferal alcohol



sinapyl alcohol



β-isopropyltropolone



catechol

More likely, partially depolymerized lignin can also provide sufficient functionality to form complexes of unusual stability and low solubility.

Compounding these trends in the affinity of certain metals for the organic constituents in coal are the secondary mineralization processes going on during maturation. For example, low levels of copper found in organic matter, despite the demonstrated stability of copper complexes prepared in the laboratory, can readily be attributed to the formation of the even more stable copper sulfide formed from sulfides generated under the reducing conditions present during coal formation.

2.5.4. Characteristics of Nonmetallic Trace Elements in Coal

In the previous sections, the major emphasis of contaminant characterization has been on the trace metals associated with coal. Of those trace nonmetallic elements important to this study, only As, Se, P, and F have been discussed and related to their possible occurrence in coal or the mineral matter in coal through correlation analysis. The elements P, F, Cl, Se, Te, and Br, however, have not been discussed in detail. A summary of the literature on the characteristics of the occurrence of these elements in coal is presented in the following discussions.

Phosphorus and Fluorine in Coal. Phosphorus in coal has been recognized as the source of phosphate-bonded deposits in superheater and reheater sections of boilers.(100) The origin of phosphorus is principally the mineral fluorapatite [$Ca_{10}F_2(PO_4)_6$] which readily loses HF when heated in moist air.(101,102) It also accounts for a major portion of fluorine in coal. Under reducing conditions and at temperatures >1590 C, elemental phosphorus is evolved which under boiler conditions is oxidized to pyrophosphoric acid, $H_4P_2O_7$. Reaction with fly-ash minerals produces crystalline phosphate deposits.

Ruch, et al(79) have isolated, photographed, and identified calcium phosphate minerals in the low-temperature ash of coals from Colorado and Illinois. Those coals, with high levels of fluorine as well as phosphorus, are considered to have the fluorapatite mineral present as well as the apatite (fluorine free) mineral. Data from analytical determinations on washed coal fractions placed phosphorus in the group of trace elements which are apparently associated both organically and inorganically in coals but are more closely allied to the elements with the higher organic affinity (along with Ga, Ti, Sb, and V). Ruch, et al(79), Abernathy and Gibson(103), and other researchers(102) could not show a strong correlation between phosphorus and fluorine in coals, but it is generally observed that coals with high phosphorus levels had high fluorine levels as well. The ratio of phosphorus to fluorine usually exceeded the weight ratio of 1.5 that would be expected for the pure fluorapatite compound, $Ca_{10}F_2(PO_4)_6$. The reason suggested was that the phosphorus may be present as the hydroxyapatite mineral or some other phosphate minerals such as $AlPO_4$.(104) The phosphate in coal is believed to be of plant origin. Mineralization yielding fluorapatite was in all probability due to fluoride diffusion from the surrounding shale coverings of the coal seam (shales are generally higher in fluorine than coal).(102) The apatite mineral is given the general formula $(RO_4)_6\ X_2\ M_{10}$, where the R is usually phosphorus but occasionally may be arsenic or vanadium. The X is usually OH or fluorine but might be chlorine or $CO_3^{=}$ ion. The M usually is calcium but may be manganese or cerium. Therefore, these trace elements may be associated with this mineral phase as well.

Coal washing was effective in reducing phosphorus in coal by 67 percent while simultaneously reducing the ash content 47 to 63 percent.(105) However, the process was successful for only two of the seven coal beds tried. For the other five coals examined, the phosphorus was associated with the "clean" coal rather than the impurities, which strongly suggests that some of the phosphorus is inherent and may be bound to the organic portion of coal. Compounds of this type have not been characterized. Similar conclusions were obtained from studies on the phosphorus content of various specific-gravity fractions separated from coals(80) and from a study on the action of sulfuric acid on phosphorus in coal.(106) No organo-fluorine compounds are considered to be present in coal, but minerals such as fluorite (CaF_2), although not identified as such, may contribute to the overall fluorine content of some coals.

Chlorine in Coal. There has been a continuous concern about the presence of chlorine (primarily as chloride ion) in coal because of inherent corrosion-related problems in steam-generation facilities associated with the element. A value for chlorine in coal from 0.15 to less than 0.40 percent is generally acceptable and should provide trouble-free operation. The chlorine content, along with the ash and sulfur contents of coals, plays an interacting role in boiler-component corrosion.

Occurrence. The manner of the occurrence of chlorine in coal has been a subject of several investigations in the United States and Europe. Two schools of thought on the subject have been cited:(107)

The manner of the occurrence of chlorine in coal has been a subject of several investigations in the United States and Europe. Two schools of thought on the subject have been cited:(107)

(1) One school postulates that the chlorine is present almost entirely as inorganic chlorides such as the salts of sodium, potassium, and calcium, and in some instances as magnesium and iron chloride.(108-111)

(2) The second school postulates that the chlorine occurs partially in combination with the organic matter in coal.(112-114)

The second school bases its argument on the fact that not all the chlorine can be removed with water and that chlorine can be driven off as HCl by heating coal in air at 200 C. The resistance to removal by water and the imbalance between soluble alkali and soluble chloride suggested that the chloride ion is attached to the coal through an ion-exchange-type association. It was also postulated that loss of chlorine below the temperature of vaporization and decomposition of inorganic chlorides could occur through organic intermediates.

Gluskoter and Rees(107) have shown experimentally that the volatilization of chlorine from NaCl could be promoted by the presence of iron pyrite (FeS_2) both in undried and dried air at temperatures below 500 C. Heating NaCl with carbon (lampblack), with clays, or alone did not produce a volatile chloride under the same conditions. Addition of NaCl to raw coal gave stronger tests for chlorine evolution than when coal was heated alone in an air stream. Strong tests were also obtained when iron pyrites and salt were heated together in air. The authors proposed that the volatilization occurred through sulfur-compound intermediates such as SO_2 and SO_3 and that there was no evidence for organically combined chlorine.

In the same study, it was found that the amount of water-soluble chlorine could not be made to equal the total chlorine contained in the coal, even with further grinding and prolonged leaching with fresh water (7 days). The reasoning given to explain this behavior was that the chloride salts were present in the very small pores in coal (most frequent size pores were near 40 angstroms in diameter), and grinding even to 5-micron particle size, although enhancing the amount of salt dissolved in water, could not produce total access to water. It was also substantiated that the established correlation used in coal analysis of relating total alkali metal to the chlorine found in coal could be used as a valid approximation. If all of the chlorine in coal were present as chlorides of sodium and potassium, the mole ratio of Na + K to Cl would be one. Ratios of 1.527 to 0.787 were found for various coals. A ratio greater than unity would mean an excess of Na and K was present. A ratio less than unity would mean a deficiency of Na and K. To explain these observations, it was suggested that other cations were associated with chlorine. The presence of Na and K ions in silicates accounts for the ratios greater than unity. The distribution ratio in the water-soluble portion of chlorides did not always agree with that found in the coal, as shown in Table 44.

TABLE 44. RATIO OF Na + K TO Cl IN COAL AND SOLUBILIZED CHLORIDE SALTS (107)

	Ratio of Na + K to Cl	
	Total Chlorine	Water-Soluble Chlorine
Illinois Coal 1	1.5268	0.8541
Illinois Coal 2	0.9302	0.1476
Illinois Coal 3	0.7866	0.5959

The ratios less than unity were claimed to be due to the presence of metal ions other than sodium or potassium. The presence of metal ions in salts such as Mg(OH)Cl and Ca(OH)Cl and minerals such as chlorapatite $[Ca_{10}(PO_4)_6Cl_2]$ has been suggested, in addition to $MgCl_2$ and $CaCl_2$.(115) Organic chlorine hydrolyzable in hot water, acid, or alkali was also postulated as a source of chloride ion. Experimental programs to prove or disprove the presence of organic chlorine in coal have been inconclusive.

A direct correlation (0.93 correlation coefficient) of the chlorine in coal versus the chlorine in groundwater has been calculated for coals of the Illinois basin.(107) This fact supported the hypothesis that the chlorine content of the coals is controlled by the composition of the groundwater in contact with the coal. A good correlation has been demonstrated between the increase in saline content of groundwater with depth and the chlorine in coals. This concept has been used to explain the trends in chlorine content of European coal beds at various depths above salt beds. There is another opinion that relates the salt content of coal to the extent that inorganic chlorides were absorbed by the plants that produced the coal prior to coal formation. The existence of chlorinated organic compounds in coal has been all but ruled out.

Removal of Chlorine from Coal. Washing of coal has been suggested as a method for the removal of chlorine from coals. It has been shown on a laboratory scale and also in field trials that only a small but variable percentage of chlorine can be readily extracted with water.(107) In a coal-washing segment of a preparation plant, fresh water with a dissolved solids content of 0.03 percent by weight was used for a period of 2 weeks. After 48 hours, the dissolved-solids level reached 0.23 percent and remained at this equilibrium level. During the operation, the chlorine in the washed coal was unaltered and identical to that in the unwashed coal. The extent of chlorine removal by washing varied for different coals. A final freshwater flushing of the washed coal reduced the chlorine content slightly, and this certainly is applicable only in those cases where the dissolved salts in the water are at low levels. Therefore, use of water recycled from settling ponds would not be effective since the dissolved salt levels would be high. It has been suggested that the practice of adding $CaCl_2$ or NaCl to prevent freezing during transportation could shift a marginal chloride level in coal to levels that may cause corrosion problems.

The experiments cited by Gluskoter and Rees did suggest that during pyrolysis or gasification (air), the chlorine content in the coal might be reduced through the formation of volatile chloride compounds in the presence of sulfur oxides. The characteristics of these volatile chloride compounds were not described.

In a study cited by Kear, et al,(115) the use of tetralin (a known hydrogen-transfer agent for coal liquefaction) produced an appreciable amount of HCl during the extraction of a high-chlorine British coal. The conclusion was that hydrogenation of chlorides that normally are insoluble had occurred. It did not necessarily mean that an organic chloride had been decomposed. However, regardless of the source of chlorine, the corrosive effects of HCl formed during any hydrogenation process involving chlorine-containing coals would have to be dealt with.

Selenium and Tellurium in Coal. Selenium is one of the elements that is found to be enriched in coals over that found in the earth's crust. This was true not only for coals of the Illinois basin but also for coals from the eastern and western United States.(80,83) Analysis of four specific-gravity fractions for selenium suggests that it is contained in both the organic and inorganic components in coal. It has been suggested that the portion in organic matter is there as an inherent selenium that was concentrated during plant growth. However, that portion associated with the sulfide and polysulfide impurities suggests that a major amount is found in the inorganic phase.(80)

Tellurium was found to be present in 85 percent of the coals analyzed by spark-source mass spectrometry in the range of <0.1 to 0.4 ppm by weight.(83) It was not reported in the 101-coal study, even though it is suited to neutron-activation analysis and flameless atomic adsorption spectroscopy.(80)

To our knowledge, the exact nature of the occurrence of tellurium in coal has not been reported. Since the ranges of selenium and tellurium levels in coal are similar, as are their chemistry, it might be expected to be distributed in the same way in which selenium is. Their dual occurrence in the residues from electrolytic copper refining muds suggests their close association with chalcopyrite (sulfide) minerals.(116)

Bromine and Iodine in Coals. Bromine has been determined in coals by X-ray fluorescence and neutron-activation analysis, while iodine has been found by neutron activation.(80,85,86,117,118) The nature of their occurrence in coal has not been described. However, the occurrence of bromine and iodine in deposits of NaCl or brines, in seawater, and in salt-lake brines is well known. The uniformity of the ratio of chlorine to bromine and chlorine to iodine in coals shown in Table 45 suggests that their origin may be the same as that of chlorine. There does not appear to be good correlation to the ratios observed in seawater or salt-lake brines; however, there is reasonable correlation in the ratio of chlorine to bromine in salt deposits. One might speculate that bromine and iodine are present principally as impurities in the inorganic chloride salts present in coal.

TABLE 45. RATIOS OF Cl, Br, AND I FOUND IN COAL AND HALIDE SOURCES

Number of Coal Samples	Range of Concentration, ppm			Ratios of Minimum and Maximum Values				Reference Cited
				Cl/Br		Cl/I		
	Cl	Br	I	Min.	Max.	Min.	Max.	
13	8-1,500	0.1-23	0.1-4	80	65	80	375	82
101	100-5,400	4-52	-	25	103	-	-	80
RR(a)	750	20	2.8	38	-	268	-	85
RR	800	17	-	47	-	-	-	86
48	320-1,400	8.2-24(b)	1.4-4.1	39	58	228	341	117
Halide Sources								
Salt brines	60.6(c)	0.05-0.30	-	1,210	202	-	-	-
Lake brines	141,000-155,000	100-160	-	1,410	968	-	-	-
Seawater	19,000	65	0.06	292	-	1,083	-	-

(a) RR = NBS-EPA round-robin sample.

(b) Bromine concentrations of 6,900 and 5,800 ppm were found in two coal samples from Belgium.

(c) Values in percentage of salt (NaCl) in Michigan brines.

2.6. Characteristics of Trace Elements in Liquid Fuels (i.e., Petroleum, Tar Sand Oils, and Shale Oils)

Liquid fuels and the characterization of the trace elements they contain are limited in this study to the liquids to be used as a feedstock to refineries and the liquids recovered from tar sands during bitumen separation or from oil shale during retorting. Therefore, in the case of petroleum, the trace elements in the crude oil as it comes from the ground are characterized. For tar sand oils, the trace elements in only the raw bitumen feedstock are characterized here. Finally, for shale oil only the trace elements prior to refining are characterized here. Similarities that exist in the characteristics of nitrogen and sulfur contaminants in the three liquid fuels are also true for the characteristics of the trace elements they contain.

As they are removed from the ground, the differences in the amount of inorganic matter associated with the fuels have been amply documented. Petroleum contains inorganic matter that is measured by its ash content. The major effort has been centered on the oil-soluble inorganic constituents, usually metals, even though the water associated with the crude contains dissolved salts. Contaminants are also introduced during well drilling and transport of the oil. Typically the range of ash content is from 0.001 to 0.130 percent and has been reported for 25 petroleums.(119,120)

Tar sands typically contain about 11 percent oil and 5 percent water by weight, with mineral matter making up the remainder. The mineral matter, which is mostly quartz sand and clays, contains numerous other mineral constituents that range in particle size up to 99.9 percent finer than 1000 microns. Particles as fine as 2 microns are also present.(12,120,123) An 85 to 90 percent recovery of bitumen from the tar sands is common practice.(19) Canadian tar sands are better characterized than are the deposits in the United States.

Oil shale is a term that refers to a wide variety of laminated sedimentary rocks containing organic matter than can be released only by destructive distillation. The mineral content of oil shale is inversely proportional to the organic matter it contains and ranges from 67 to 92 percent. The major minerals (95 percent of the total minerals) are dolomite, calcite, quartz, and feldspars.(41,124) Minor mineral constituents are clay minerals, pyrite, and analcite.(16,124,125) The mineral matter is extremely finely divided (90 percent <44 microns).(124) Typically, about 66 percent of the organic matter is obtainable as liquid or shale oil, regardless of the retorting procedure.(19,124) About 9 percent ends up as gaseous hydrocarbons. Contact between the organic matter (kerogen) and the inorganic mineral matter is limited to the external particle surface, and micropore structure is considered insignificant.(16) Kerogen, the major organic constituent of oil shale, has been concentrated by centrifugation after removing the inorganic material. Organic sulfur and nitrogen compounds were found to be only weakly bound to the mineral constituents. Oxygen compounds were more closely associated with the kerogen and not with the mineral matter. Iron compounds other than pyrites were found to be closely associated with the organic material.(125)

2.6.1. Trace Elements Identified in the Liquid Fuels

This section will point out the influence that new analytical techniques have had on identifying trace elements in liquid fuels. Major emphasis has been put on the elements associated in petroleum, primarily those considered to be oil soluble. Efforts to identify trace elements in the bitumin extracted from tar sands and the liquids retorted from shale oil have not been as extensive as those for petroleum.

Trace Elements in Petroleum. Most analyses for trace elements in petroleum have been done on the ash obtained from the oxidation of petroleum samples and each constituent is usually reported as the percentage in ash. Early spectral analyses were semiquantitative at best, except for the elements V, Ni, Cu, and U.(120) Chemical analysis of ash provided quantitative values for Ni, Na, Si, V, Fe, Al, Ca, and Mo (SO_3 values were also determined).(119) Typical values obtained for 24 petroleums using spectrographic analysis are given in Table 46.(120) Chemical analysis of the ash from 25 other petroleums exhibited a wide range of values and are reported as percentage of oxides in the ash in Table 47.(119)

TABLE 46. DISTRIBUTION OF 28 TRACE METALS IN ASHES OF 24 CRUDE OILS(120)

Metal	Occurrence in Percent of Samples	Concentration Range in Ash,(a) Percent	Concentration Range(b)	
			Percent of Ash	ppm in Crude
Al	100	0.001 - 10		
Fe	100	0.01 - >10		
Ti	50	0.001 - 1.0		
Mn	96	0.001 - 1.0		
Ca	100	0.01 - >10		
Mg	100	0.1 - 10		
Na	88	0.1 - >10		
K	8	1 - 10		
Ag	17	0.1 - 1		
As	21	0.001 - 1		
B	17	0.001 - 1		
Ba	100	0.001 - 1		
Ce	33	0.01 - 1		
Co	100	0.001 - 1		
Cr	100	0.001 - 0.1		
Cu	100	0.001 - >10	13 - 0.007	1.7 - 0.03
Ga	67	0.0001 - 0.01		
La	38	0.001 - 1		
Mo	83	0.001 - 1		
Nd	8	0.1 - 1		
Ni	100	0.01 - >10	16 - 0.1	35 - 0.03
Pb	96	0.001 - 1.0		
Sn	38	0.001 - 1.0		
Sr	92	0.0001 - 1.0		
V	100	0.001 - >10	46 - 0.41	106 - 0.002
Zn	58	0.01 - 10		
Zr	33	0.001 - 1.0		
U	100	0.0001 - 0.01	0.0075-0.001	0.013-0.00012

(a) Semiquantitative values.

(b) Quantitative values.

TABLE 47. SUMMARY OF THE ANALYSIS OF OIL-SOLUBLE ASH IN 25 CRUDE OILS(119)

(Range of Ash, wt % = 0.005 to 0.0388)

	Ash Chemical Analysis,[a] weight percent
NiO	0.1 to 17.9
Na_2O[a]	3.0 to 46.5
SiO_2	0.9 to 11.7
V_2O_5	0.1 to 64.9
Fe_2O_3[a]	0.3 to 29.0
Al_2O_3	0.5 to 12.1
CaO	1.1 to 33.2
SO_3	0.2 to 59.6

(a) Na_2O and Fe_2O_3 were found in all samples.

Other methods such as X-ray fluorescence, atomic adsorption, electron paramagnetic resonance, and plasma arcs have been used for trace-element analysis. The limited sensitivities of these methods require concentration of the samples (usually by ashing) before analysis. Such treatment creates the situation where potential contamination of samples or volatilization of compounds and elements such as Cl, Br, S, Se, As, and Hg might occur. In addition, analysis of the whole petroleum or petroleum fractions without altering the sample by concentration provides added latitude in the characterization of these trace elements in their unaltered state. With the development of neutron-activation analysis using high-resolution spectrometry (INAA), a rapid nondestructive analysis for Na, S, Cl, K, Ca, V, Mn, Cu, Ga, Br, Sc, Cr, Ni, Co, Zn, Se, As, Sb, Eu, Au, Hg, and U is now readily made.(124,125) Special techniques permit the INAA determination of cadmium.(128) Others have expanded the technique to include analysis for In, La, and Sm.(129) Less sophisticated nuclear-activation techniques require radiochemical separation for the determination of only one element at a time, but have been used to characterize the trace elements in petroleum fractions and develop contaminant correlations. It should be noted here that neutron-activation analysis provides the means for the analysis of nonmetallic elements as well as metals.(130,131) The results of INAA analyses performed on four crude oils are given in Table 48. The detection limits in parts per billion (ppb) for 22 elements are given in Table 49.

Germanium, although capable of being detected by INAA, has not been reported in oil using the activation method. However, germanium has been reported in oils in the USSR and its behavior has been characterized.(131) Rhenium has also been reported to be present in both oils and heavy oils, in bitumins, and in oil shale of the USSR in the range of 5 to 200 ppb for the oils and 5 to 800 ppb for bitumens.(132) Fluorine has been reported to be present in ten crudes. The range of fluorine in oils is 0.14 ppm for Iranian heavy crude to 1.1 ppm for Alaskan crude. Forty-two crude oils representing 90 percent of the oils used in West Germany were found to contain less than the detection limit of 0.03 ppm fluorine (ion selective electrode).(133,134)

TABLE 48. TRACE-ELEMENT CONTENTS OF FOUR CRUDE OILS OBTAINED BY NEUTRON-ACTIVATION ANALYSIS(128)

	Concentration in Crude Oil(a)			
Element	California (Tertiary)	Libya	Venezuela (Boscan)	Alberta (Cretaceous)
V	7.5	8.2	1100	0.682
Cl	1.47	1.81	-	25.5
I	-	-	-	-
S	9.90	4694	-	1450
Na	13.2	13.0	20.3	2.92
K	-	4.93	-	-
Mn	1.20	0.79	0.21	0.048
Cu	0.93	0.19	0.21	-
Ga	0.30	0.01	-	-
As	0.655	0.077	0.284	0.0024
Br	0.29	1.33	-	0.072
Mo	-	-	7.85	-
Cr	0.640	0.0023	0.430	-
Fe	68.9	4.94	4.77	0.696
Hg	23.1	-	0.027	0.084
Se	0.364	1.10	0.369	0.0094
Sb	0.056	0.055	0.303	-
Ni	98.4	49.1	117	0.609
Co	13.5	0.032	0.178	0.0027
Zn	9.76	62.9	0.692	0.670
Sc(a)	8.8	0.282	4.4	-
U	-	0.015	-	-

(a) Values in ppm, except for scandium which is given in ppb.

TABLE 49. DETECTION LIMITS FOR DIFFERENT ELEMENTS IN A "TYPICAL" CRUDE OIL MATRIX IN PPB(128)

Element	Detection Limit	Element	Detection Limit
Cl	10	Ni	30
S	1000	Co	0.02
V	2	Se	23
Na	20	Hg	4[a]
As	6	Zn	90
Ca	4000	Cr	23
Mn	15	Fe	400
Cu	100	Sb	1.0
Ga	25	Sc	0.1
Br	1.5	U	100
I	5	Mo	500

(a) Assumes selenium absent.

Of the elements cited for this study, analytical values for Te, P, and Be have not been reported for petroleum. A summary of the 42 trace elements found in petroleum is given in Figure 11. Similar compilations made on the basis of much earlier work mentioned other elements, e.g., Li, Be, P, Pb, Y, Tl, and Bi but did not include any of the halogens.(135)

Trace Elements in Tar Sand Oils. Tar sand oils (or the raw bitumin before it undergoes upgrading) contain various amounts of ash which appear to vary with the bitumen-recovery process. Typically the ash content can range from 0.65 percent by weight (700 C) to as high as 3.5 percent.(136,137) Much of the ash is due to residual concentration of clay and silt. The concentration of nickel and vanadium in the bitumen with a low ash content was 68 and 189 ppm, respectively, while the concentration levels of these elements in the bitumen with the high ash content were 70 and 180 ppm, which suggests that the residual clays and silt only contribute ash without affecting the nickel and vanadium concentrations. Trace elements attributed to the mineral matter associated with tar sands are assumed present. Copper concentration in the Athabasca bitumen is about 5 ppm. Utah tar and oils contain 10 ppm of vanadium and 88 ppm nickel.

Trace Elements in Shale Oil. Shale oil which has been recovered after retorting has a small amount of entrained shale mineral matter. Sediments of the order of 0.04 weight percent have been reported.(19) Elements present in the shale mineral matter are also present in the crude shale oil. Trace amounts of nickel (4-6 ppm), vanadium (1.5 to 6.0 ppm), and iron (55-108 ppm) have been found in Colorado crude shale oils from three retorting processes. Recently, arsenic has been reported in shale oil at a concentration of 40 ppm.(138) The same study identified the following oil-soluble elements in shale oil: Sb, Be, B, Cd, Ca, Cr, Co, Cu, F, Ge, Pb, Mg, Mn, Hg, Mo, K, Se, Ag, Na, Sr, Te, Ti, V, Y, and Zn.

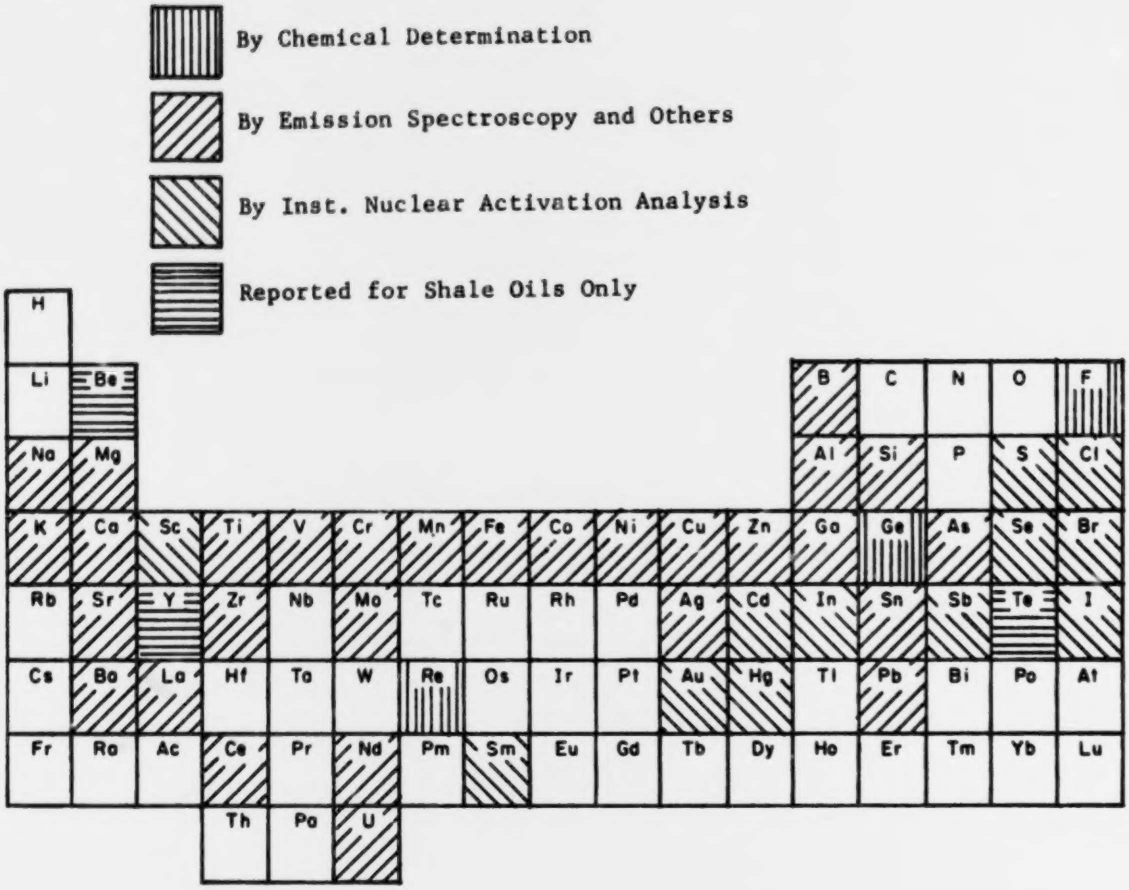

By Chemical Determination
By Emission Spectroscopy and Others
By Inst. Nuclear Activation Analysis
Reported for Shale Oils Only
H
Li Be B C N O F
Na Mg Al Si P S Cl
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br
Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I
Cs Ba La Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At
Fr Ra Ac Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
Th Pa U

FIGURE 11. TRACE ELEMENTS IDENTIFIED IN PETROLEUM AND SHALE OILS

2.6.2. Trace Elements Associated with Petroleum Mineral Matter

Except for petroleum which inherently has low mineral content (except for the associated brines), the two other principal liquid fuels, tar sand oils (bitumins) and shale oils, have been separated from their host minerals. However, residues and entrained minerals contribute to the overall trace-element concentrations. This is also true in the case of petroleum. The water commonly associated with petroleum contains dissolved salts. Portions of the Ca, Mg, and Na values found in the ash from petroleum have their origin as NaCl, $CaCl_2$, and $MgCl_2$ dissolved in the water. In addition, emulsified water present in the crude contributes to the overall contaminant level.(119,139,140) The determination in crude oils of 1.5 to 25 ppm chlorine along with bromine (0.12 to 1.5 ppm) and iodine (0.12 to 1.5 ppm) by neutron-activation analysis supports this possibility.(26,140)

Brine is associated with crude oil both as a fine suspension of droplets and as more permanent emulsions. The demarcation line between these two types is not always clear, but, generally, the less stable mixtures can be separated by simple settling methods, whereas the more permanent mixtures require chemical or electrical methods.(141)

Relatively little has been published on the amount of salt contained in crude oils, and little consistency in values is evident because the brine which contains the salt tends to settle from the crude oil during handling. Thus, the salt content of oil at the field is higher than the salt content at the pipeline or at the refinery. Neither crude oil gravity nor bottom sediment and water content appear to be related to salt content except when in a particular field or region. Some typical salt contents of crude oils from various regions are shown in Table 50.

The removal of brine from crude oil is important because the salt can leave deposits on processing equipment, thus leading to fouling or plugging of heat exchangers. The salt also increases the coking rate when the crude oil is heated, such as in the initial distillation operations.

TABLE 50. TYPICAL SALT CONTENTS OF CRUDE OILS(141)

Region	Lb Salt Per 1000 Bbl		Number of Samples
	Average(a)	Range	
Pennsylvania	1	--	6
Wyoming	5	1-13	8
Middle East	8	1-1,085	9
Venezuela	11	0-63	124
East Texas	28	9-44	5
Gulf Coast	35	2-70	11
Pipelines (U.S.)	65	22-200	12
Oklahoma and Kansas	78	7-305	15
Canada	200	10-8,250	14
West Texas	261(b)	4-2,580	173

(a) Very high samples omitted from average.

(b) Most samples taken at field.

Also, the chloride salts (particularly $MgCl_2$) tend to decompose during processing of the oil, thereby liberating HCl and contributing to corrosion problems. The combination of HCl and H_2S is particularly troublesome in this regard. Reduction of the salt content to 15 to 30 g/1000 liters (5 to 10 pounds per 1000 bbl) of crude oil greatly reduces corrosion problems.(141)

2.6.3. Trace Elements Associated with Petroleum Organic Matter

Shale oil and more so tar sand oils are similar to petroleum in that the major portion of the trace elements associated with them are present in the organic phase. In other words, the contaminants are oil soluble or in oil suspension. The following constituents are present in minor amounts in the three liquid-fuel types:

- Heterocyclic organic compounds containing sulfur, nitrogen, and oxygen (i.e., nonhydrocarbons)
- Inorganic substances such as silica, salts, and metals
- High-molecular-weight asphaltic molecules.

Despite their low concentrations, these constituents are the source of environmental pollutants and the cause of corrosion of equipment and poisoning of catalysts. In the refining process, the raw fuel is treated to eliminate these constituents, usually by chemical conversion and upgrading. The processes of desulfurization, denitrification, and demetallization ensure a clean final fuel. Reductive cleavage of the heterocycles removes the heteroatoms by the splitting of the heteroatom-carbon bonds into H_2S, NH_3, and H_2O. The asphatenes are usually depolymerized during the hydrodesulfurization process. Removal of metallic impurities can be done by acid treatment or by a process that employs a slurry of asphaltenes.(139) In the area of trace-element contaminants in petroleum, major emphasis has been placed on the characterization of the trace metals.

Background on the Characterization of Trace Metals in Petroleum.

Petroleum, although it consists predominantly of hydrocarbons, also contains measurable quantities of metals. Nickel and vanadium are commonly most abundant. In addition, Fe, Zn, Cr, Cu, Mn, Co, and others are almost always present in concentrations from less than 1 ppb to more than 100 ppm.(139) Characterization based on groups of metals present in crudes and ratios of metal concentrations have been made to aid in correlation of the age and depth of oil deposits and in some cases their countries of origin. Much work has been done in the interpretation of trace-element data for development of valid geochemical interpretations. To do this it is necessary to know in what forms trace elements occur. Except for nickel and vanadium, such information is lacking. It is a generally accepted fact that metals may be present in crude oil as inorganic particulate matter (such as mineral grains, or absorbed on clay minerals), in emulsified formation waters, introduced in drilling fluids and corrosion inhibitors, or present in oil solution as metal complexes of organic ligands. The characterization here deals only with the oil-soluble forms of metals.

Significant amounts of nickel and vanadium cannot be accounted for by free metalloporphyrins in crude oils. Both vanadium and nickel concentrations increase with asphaltic content of the oil (API gravity), and lighter oils contain less metals. Usually, the vanadium concentration is higher than the nickel concentration but this is not always the case.(139)

Yen classified metal components in petroleum into the following categories:(139)

(1) Metalloporphyrin chelates
  (a) Compounds with heterocyclics containing nitrogen, e.g., vanadyl and nickel porphyrins.
  (b) Chlorophyl *a* and other hydroporphyrins.
  (c) Highly aromatic porphyrin chelates.
  (d) Porphyrin decomposition ligands.

(2) Transition metal complexes* such as those of V, Ni, Fe, Cu, Co, and Cr of tetradentate** mixed ligands
    (a) Simple complexes from resin molecules
    (b) Chelates** from asphaltene sheets

(3) For organometallic compounds of such elements as Hg, Sb, and As, both alkyl and aryl types are possible as are π-complexes.

(4) Carboxylic acid salts of polar functional groups of the resin component with elements like molybdenum or germanium in coal. Complexes of α-dihydroxyl groups of catechol, thiocarboxylic acids, and N-containing ligands are possible.

(5) Colloidal minerals such as NaCl or silica carried over by water during formation and other fluids introduced during oil recovery.

The two major classes of metals considered to be important are the porphyrin metals and nonporphyrin metals. Porphyrin metals have been studied widely. Nonporphyrin metals have not been as extensively characterized, and typically in these compounds, the porphin skeleton has lost its true porphyrin characteristics as reviewed by Yen.(139) As seen in Figure 12, the basic porphin structure with uninterrupted conjugation is repeated in chlorophyl-a and the deoxyphylloerthroetioporphyrin (DPEP) and etioporphyrin-III forms of vanadyl complexes (nickel complexes are similar). Porphyrin systems vary extensively because of substituents, isomers, and symmetry differences as well as with the central metal atoms they contain. Altered or modified porphyrins such as hydroporphyrin, arylporphyrin, and degraded porphyrin products all fall under the nonporphyrin systems containing complexed metals.

The other major class of nonporphyrin metals comprises the compounds forming complexes of the tetradentates type with mixed ligands usually

---

* Complexes refer to compounds with more than one ligand molecule to one metal atom.

** Chelates refer to compounds in which one ligand satisfies the coordination sites ($\geq 2 \leq 6$) of one central metal atom, e.g., tetradentate liqand provides 4 coordination sites per molecule.

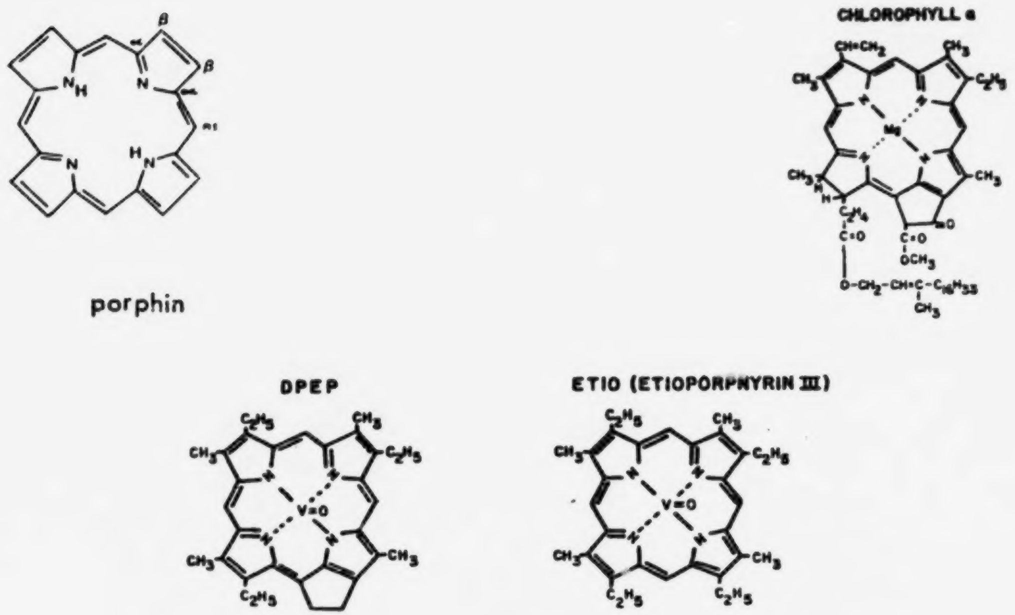

porphin
CHLOROPHYLL a
DPEP
ETIO (ETIOPORPHYRIN III)
V=O
Mg

FIGURE 12. THE PORPHIN STRUCTURE AND WELL KNOWN PORPHYRINS CONTAINING THE STRUCTURE(139)

containing a combination of N, S, and O heteroatoms. Some of these are shown in Figure 13. Smaller molecular systems are usually formed from the resin molecules and larger systems are formed from the asphaltic sheets that are known to contain these heteroatoms. Yen(139) has given supporting evidence for the existence of tetradentate ligand-metal complexes in both the resin and asphaltene components of oil.

During the genesis of asphaltenes, it has been postulated that the graphitization process is interrupted owing to the presence of nitrogen, sulfur, and oxygen atoms.(139) Therefore, a structure consisting mostly of fused benzene rings exists; however, holes or gaps in the hexagonal array are formed where these heteroatoms are located. This is represented graphically in Figure 14.(142) Such holes or gaps provide sites for metal-complex formation and metals held as these complexes cannot be removed by aqueous acid washing. Metals can be removed from the tetradentate complexes present in the resin component of oil under slightly acid conditions.

Characterization of Trace-Metal Contaminants by Physical Separation. A physical separation of petroleum into various fractions has been done by ultracentrifugation in an attempt to characterize the colloidal nature of petroleum.(140) This method of separation provided a means to limit the amount of polar molecules normally removed with the asphaltene component of petroleum by n-propane precipitation (as described later). Therefore, metal constituents, salts, water, and other metals, including those normally dissolved in oil (yet polar), are not precipitated and may be better correlated to their true existence in petroleum. The following findings were cited as important in characterizing the trace-element contaminants in petroleum, especially as it relates to the colloidal material.(140)

- Most metals were found to be associated with the colloidal material. The colloids are rich in asphaltenes, vanadium, nickel, and nitrogen. The bottom one-third of the centrifuged sample contained 10 percent asphaltene and 42 percent nonhydrocarbon (feed: ~7 percent asphaltene).

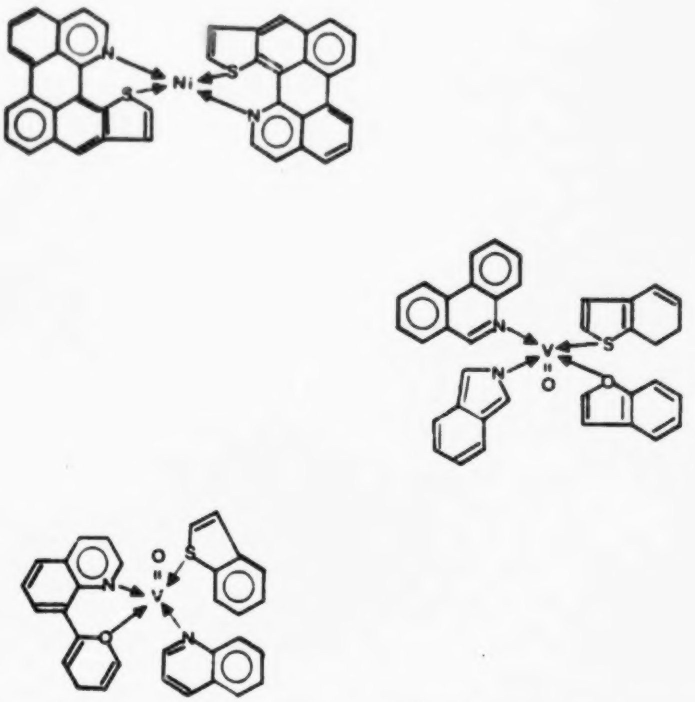


FIGURE 13. TETRADENTATE METAL COMPLEXES OF NICKEL AND VANADIUM WITH MIXED LIGAND ATOMS(139)

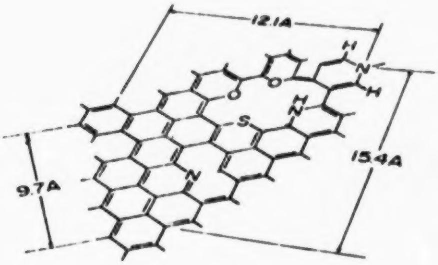

12.1A
15.4A
9.7A
S
N
O
H

FIGURE 14. MODEL DEFECT SITE (OR GAPS) IN AN AROMATIC SHEET OF THE ASPHALTENE STRUCTURE(142)

- Sulfur (and nitrogen) correlates well with asphaltene content; metals show a linear relationship (see Figure 15) The authors suggested that if oil were freed of asphaltene, only 2 ppm metals would exist in true solution. Sulfur does not exhibit a linear relationship to asphaltene content as the metals do. This was attributed to the high solubility of some sulfur organic components not present in the asphaltenes.

Although this technique showed that metal, sulfur, and nitrogen contaminants could be partitioned, sample sizes were too small for characterizations that are possible by solvent precipitation techniques. The results do lend support to Yen's concepts and reasons for the investigation of a centrifugal process for metal removal.

Effect of Filtration and Water Washing on Crude-Oil Metal Content. Filtration of benzene-diluted crude yielded black deposits that exhibited only background levels of trace elements. Analysis of unfiltered and filtered crudes from California and Venezuela showed significant decreases in arsenic and sodium, and mercury, iron, arsenic, and sodium, respectively, after filtration. An aqueous phase separated from the California oil contained 2800 ppm sodium, 21.3 ppm iron, and 18.2 arsenic and appeared to be residual water retained by the crude. Negligible amounts of other elements could be ascribed to the aqueous phase.

Distilled-water extraction of California oil indicated that 92 percent of the sodium, 37.5 percent of the arsenic, and 22.5 percent of the antimony were extracted, but other elements were not affected. Repeated extractions did not alter the sodium, arsenic, and antimony levels remaining in the oil. This and related data supported Filby's conclusion that the sodium in these oils was there as an oil-soluble compound or one that is readily hydrolyzed (sodium salt of petroleum acid).(143) In addition, some of the arsenic and antimony appears to be present as soluble or readily hydrolyzable compounds.

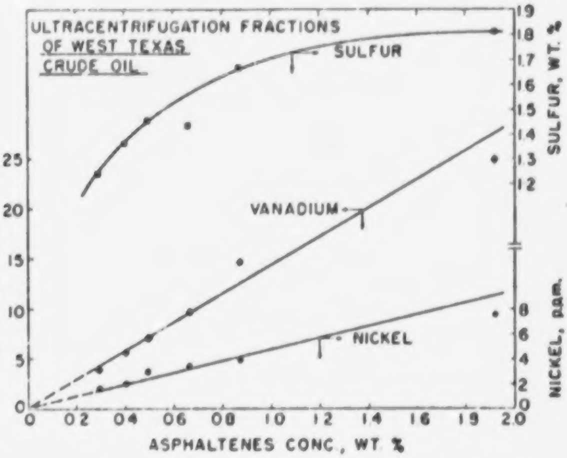


FIGURE 15. EFFECT OF ASPHALTENES CONTENT ON SULFUR AND METALS IN SIX FRACTIONS OF ULTRACENTRIFUGED OIL(140)

Characterization of Trace-Metal Contaminants by Solvent Precipitation. The liquid fuels, especially petroleum, have been characterized by separation into their components based on the solubility of each component in a series of solvents. Several approaches have been used, but one that appears to be well suited to trace-element characterization is the following scheme and definitions:(143-145)

n - pentane insoluble = asphaltenes
n - pentane soluble but methanol insoluble = resins
methanol soluble = methanol solubles.

Further separation of each of the components and chemical characterization of these isolated fractions have been done for the purpose of locating the centers of contaminant concentration. For example, both the resins and the asphaltenes are minor components in oil, yet they contain a proportionately large fraction of the nitrogen and sulfur contents of crude oils (10 to 50 percent), as shown in Table 51.(139,143-145) In addition, the distribution of metal contaminants in each of the components of petroleum as complexes of organic molecules called porphyrins or as nonporphyrin compounds have also been determined. Recent publications on the subject have drawn extensively on review of past work and provide an up-to-date interpretation of the characteristics of trace metals in petroleum. Much of the information that follows is covered in articles by Filby(143) and Yen.(139)

A California tertiary crude oil, which has high trace-metal concentrations, has been characterized as to the distribution of the trace metals within each component of petroleum and the distribution of the metals within various molecular-weight fractions of each component. The capability of neutron-activation analysis to determine metal concentrations on small (0.1 to 1.0 g) samples was fundamental to this study by Filby.(143) The distribution of V, Co, Hg, Fe, Zn, Cr, As, Sb, Na, and Cd was determined in the asphaltene, resin, and methanol-soluble components of petroleum. Further separation of these three components into fractions with four molecular-weight

TABLE 51. DISTRIBUTION OF PERCENTAGE OF TOTAL NITROGEN OF CRUDE IN RESINS AND ASPHALTENES(139)

Crudes	Percent of Crude		Percent Nitrogen		Percent Sulfur	
	Resin	Asphaltenes	in Resins	in Asphaltenes	in Resins	in Asphaltenes
Mara-La Lune	9.1	4.1	30.0	27.5	20.5	10.5
Oficina	3.9	1.1	18.3	12.8	33.3	13.8
Ragusa	9.2	0.28	--	48.2	--	24.3
Wilmington	14.2	5.1	30.5	15.6	22.9	8.5
North Belridge	18.0	5.1	25.8	14.8	23.9	7.8
Boscan	29.4	18.0	20.4	41.0	35.1	23.0
Sandhills	4.4	0.44	8.5	3.2	9.1	3.1
Abell-Ellenburger	4.2	0.24	39.3	3.1	33.8	3.9
South Waddell	3.9	0.39	50.0	10.0	17.4	3.1
Keystone	2.2	0.22	40.0	10.0	15.1	0.34
South Ward	1.2	0.80	14.4	3.9	6.7	2.3
Hiseville	0.97	0.19	53.0	4.1	12.2	0.7
Athabasca	24.2	19.4	21.8	49.7	28.2	28.5

ranges was accomplished by gel-permeation chromotography (GPC). Liquid chromotography was also used to separate porphyrin concentrates in an attempt to determine whether metal porphyrins other than those of nickel and vanadium existed. Several other crude oils with high (>5 percent) asphaltene content as well as high trace-metal concentrations were among those selected for study.

Effect of Filtration and Water Washing on Crude-Oil Metal Content. Filtration of benzene-diluted crude yielded black deposits that exhibited only background levels of trace elements. Analysis of unfiltered and filtered crudes from California and Venezuela showed significant decreases in arsenic and sodium, and mercury, iron, arsenic and sodium, respectively, after filtration. An aqueous phase separated from the California oil contained 2800 ppm sodium, 21.3 ppm iron, and 18.2 ppm arsenic and appeared to be residual water retained by the crude. Negligible amounts of other elements could be ascribed to the aqueous phase.

Distilled-water extraction of California oil indicated that 92 percent of the sodium, 37.5 percent of the arsenic, and 22.5 percent of the antimony were extracted, but other elements were not affected. Repeated extractions did not alter the sodium, arsenic, and antimony levels remaining in the oil. This and related data supported Filby's conclusion that the sodium in these oils was there as an oil-soluble compound or one that is readily hydrolyzed (sodium salt of petroleum acid).(143) In addition, some of the arsenic and antimony appears to be present as soluble or readily hydrolyzable compounds.

Distribution of Metals in the Three Isolated Petroleum Components. Analyses of the asphaltene component revealed that it contained the highest concentrations of all elements, and that the combined resin and asphaltene fractions (i.e., the asphaltic components) account for the major portion of the trace elements V, Ni, Co, Fe, Hg, Zn, Cr, and Sb in California oil. Table 52 shows the distribution of the trace elements among the three components separated from this crude oil, and the ratios of the asphaltene to

TABLE 52. DISTRIBUTION OF TRACE ELEMENTS IN COMPONENTS OF A CALIFORNIA CRUDE OIL(143)

Trace Element	Trace Element Concentration, ppm				Ratio of Trace Element Concentrations	
	Crude Oil	Methanol Soluble	Resins	Asphaltenes	R/C[a]	A/C[b]
Crude Oil, percent	100.0	57.5	37.5	4.99		
V	7.5	0.82	12.4	61.6	1.65	8.2
Ni	93.5	7.21	147.0	852.0	1.57	9.1
Ni/V ratio	12.47	8.8	11.9	13.8		
Co	12.7	0.8	10.7	122.0	0.84	9.6
Fe	73.1	1.95	66.4	895.0	0.91	12.2
Hg	21.2	0.686	29.6	140.0	1.40	6.6
Cr	0.634	0.300	0.894	7.540	1.41	11.9
Zn	9.32	0.74	8.86	109.	0.95	11.7
Sb	0.0517	0.0033	0.0130	1.22	0.25	23.6
As	0.656	0.546	0.290	2.25	0.44	3.4

(a) R/C = ratio of concentration in resins to that in crude.

(b) A/C = ratio of concentration in asphaltenes to that in crude.

crude oil (A/C) and resin to crude oil (R/C). Of particular importance is the observation that 48 percent of the arsenic is present in the methanol-soluble fraction and suggests the presence of low-molecular-weight compounds, possibly as alkyl or aryl arsines. The elements Ni, V, Co, Fe, Cr, Hg, and Zn are enriched in the asphaltene phase. (Since it is well established that the asphaltenes and resins exist in the oil as a colloidal dispersion, the crude oil may be considered as a system of the polar aromatic micelles of asphaltenes and less-polar resins in the major, nonpolar-hydrocarbon phase of the crude oil.)(140,143)

In the separation scheme used to isolate the three oil components, the trace-element constituents enriched in the asphaltene may have their origin from the presence of small (low molecular weight), highly polar molecules which could precipitate with the asphaltenes when a non-polar solvent such as n-pentane is used. On the other hand, the metal ions might be complexed in the asphaltene sheet structure at sites bounded by heteroatoms of sulfur, nitrogen, or oxygen.

Studies by Filby(143) using gel-permeation chromotography showed the molecular-weight-fraction distribution for the three petroleum components to be that given in Table 53. The similarity of the resin and asphaltene molecular-weight distribution suggested similarity in the makeup of these two fractions. Therefore, the difference in solubility behavior in n-pentane was attributed to the greater polarity of the asphaltenes rather than to molecular-weight differences. The presence of 11 percent material with a molecular weight of 300 to 1000 suggested that small polar molecules are isolated with the asphaltene micelles during precipitation of the n-pentane-insoluble components.

The distribution of trace elements found in the various asphaltene and resin molecular-weight fractions is shown in Tables 54 and 55. These can be compared with the distribution for the methanol-soluble fractions given in Table 56. The following observations were made by Filby for the asphaltenes fractions:

TABLE 53. DISTRIBUTION OF MOLECULAR-WEIGHT FRACTIONS OF OIL COMPOUNDS(143)

Molecular-Weight Fraction	Percentage of Fraction		
	Methanol Soluble[a]	Resins	Asphaltenes
300-1,000	93.8	29.4	11.0
1,000-4,000	6.2	21.2	23.2
4,000-8,000	--	49.4	50.6
8,000-22,000	--	0	15.2
Total	100.0	100.0	100.0

(a) The higher-molecular-weight component of the methanol fraction was not separated into smaller fractions.

TABLE 54. DISTRIBUTION OF TRACE ELEMENTS IN ASPHALTENES[a] (143)

Molecular-Weight Fraction (GPC):	300-1,000	1,000-4,000	4,000-8,000	8,000-22,000	Total
Fraction, percent:	11.0	23.2	50.6	15.2	100.0
Ni	1327.0[a]	189.0	984.0	1060.0	852.0
Co	2.67	30.00	167.00	176.00	122.00
Fe	480.0	368.0	867.0	1934.0	895.0
Hg	72.0	20.9	90.0	350.0	140.0
Cr	0.77	4.80	9.12	19.6	7.540
Zn	112.00	52.00	103.00	225.00	109.00
Cu	0.34	1.50	4.00	7.20	3.02
Sb	11.0	0.9100	0.3500	0.1040	1.2200
As	0.850	0.620	1.900	6.600	2.250

(a) All values in ppm.

TABLE 55. DISTRIBUTION OF TRACE ELEMENTS IN RESINS[(a)] (143)

Molecular-Weight Fraction (GPC): Fraction, percent:	300-1,000 29.4	1,000-4,000 21.2	4,000-8,000 49.4	8,000-22,000 0	Total 100.0
Ni	206.0 (a)	110.0	80.2	-	147.0
Co	4.37	10.00	24.90	-	10.70
Fe	30.1	24.0	236.0	-	66.4
Hg	22.0	44.0	72.0	-	29.6
Cr	0.310	0.800	2.960	-	0.894
Zn	3.31	11.00	27.00	-	8.86
Cu	<0.20	<0.50	1.30	-	0.32
Sb	0.0430	0.0026	0.0054	-	0.0130
As	0.407	0.200	0.200	-	0.290

(a) All values in ppm.

TABLE 56. DISTRIBUTION OF TRACE ELEMENTS IN METHANOL-SOLUBLE FRACTIONS(143)

Molecular Weight Fraction	Total, percent	Concentration, ppm								
		Ni	Co	Fe	Hg	Cr	Zn	Cu	Sb	As
300-1,000	93.8	11.00	0.73	< 1.00	0.410	--	< 1.00	--	0.0046	0.340
> 1,600	6.2	< 1.00	2.61	9.90	7.130	--	3.50	--	<0.0020	5.000
Total	100.0	7.21	0.80	1.95	0.886	< 0.3	0.74	< 0.5	0.0033	0.564

- The highest trace-element concentrations (except nickel and antimony) were found in the highest-molecular-weight fraction.
- The highest nickel concentration was found in the 300 to 1000 molecular-weight fraction (entirely nickel porphyrins associated with asphaltenes).
- Sb concentration was highest in lowest-molecular-weight fraction and decreased with increasing molecular weight of the asphaltene component.
- Cr, Cu, and Co show increasing concentration with increasing molecular weight of the asphaltene fractions.
- Fe, Hg, Zn, and As show highest concentration in the highest-molecular-weight asphaltene fraction. The possible existence of porphyrin derivatives of these metals was surmised by the fact that their concentration was greater in the 300 to 1000 fraction than in the 1000 to 4000 fraction.

The resin fractions show trace-element patterns similar to those of the asphaltenes; however, their concentrations were much lower. In the methanol-soluble component, only nickel and antimony are present in greater concentration in the low-molecular-weight fraction (nickel as porphyrin and antimony as low-molecular-weight organoantimony compounds). The existence of Fe, Hg, Zn, and Co as porphyrins in the low-molecular-weight fraction was not ruled out, but their exact character is not known. Filby(143) has shown that about 50 percent of the nickel in the higher-molecular-weight asphaltenes is present as nonporphyrin compounds, the percentage increasing with the molecular weight of the fraction. The results of the study are given in Table 57. The same trend was observed for the resin component of crude oil. Similar trends have been observed for vanadium.(146) Data on Fe, Co, Zn, Cr, and Hg suggested that they occur as nonporphyrins in oil and that their behavior is similar to that of nonporphyrin nickel.

TABLE 57. DISTRIBUTION OF NICKEL AND NICKEL PORPHYRIN IN ASPHALTENES AND RESINS FROM A CALIFORNIA TERTIARY OIL(143)

Molecular-Weight Fraction (GPC)	Asphaltenes or Resins, percent	Nickel As Nickel Porphyrin, percent	Nonporphyrin Nickel, percent
		Asphaltenes	
300-1,000	11.2	100.0	0
1,000-4,000	23.2	49.0	51.0
4,000-8,000	50.6	34.5	65.5
8,000-22,000	15.2	22.9	72.1
Total	100.0	49.2	50.8
		Resins	
300-1,000	29.4	100.0	0
1,000-4,000	21.2	38.6	61.4
4,000-8,000	49.4	32.0	68.0
8,000-22,000	0	-	-
Total	100.0	64.0	36.0

Conclusions made by Filby on the basis of his work and the review of the work of others are as follows:

- Oil-soluble compounds of Ni, V, Fe, Co, Cr, Hg, Zn, As, Sb, Cu, and Na are present in California tertiary crude oil.
- Nickel is present in the oil as nickel porphyrin and nonporphyrin nickel. The porphyrin compounds, which are found to be present in all fractions of crude oil, accounted for 100 percent of the nickel in the low-molecular-weight fractions of the three oil components. The proportion of nickel in the resins and asphaltenes increased with molecular weight.
- The elements Fe, Co, Zn, Hg, Cr, and Cu occur in a nonporphyrin form in the oil. Porphyrin complexes of these metals were not observed. These elements are incorporated into the asphaltene sheet structure through complexing at holes bordered by nitrogen, sulfur, and oxygen atoms.
- Arsenic and antimony appear to be present as low-molecular-weight compounds such as alkyl or aryl arsines and stibines. The antimony compounds are also associated with the asphaltenes.
- The origin of the Fe, Co, Hg, Zn, Cr, and Cu in asphaltenes may involve complexing from an aqueous or solid phase (rocks) during maturation of the petroleum.

The characteristics of the nature of vanadium compounds contained in petroleum have been the subject of numerous studies and reviews.(142,144,147-150) These studies conclude that there are a number of types of vanadium compounds in petroleum and virtually all are complexes. Since they are readily separated by extraction, much work has been directed toward detecting their presence. The commonest of these are the porphyrins. Other types of complexes exist such as the tetradentate mixed ligands containing nitrogen, sulfur, and oxygen donor atoms, and pseudoaromatic and highly aromatic porphyrins.

(Association with asphaltenes through π-electron bonding has been postulated.)(150) These latter complexes are held tightly in the organic matrix and as a result exert a strong influence on the properties of petroleum samples. Vanadium's adverse effects in refining and on health are also well documented.

Mechanisms for Trace-Metal Removal from Petroleum. The removal of trace metals from petroleum is complicated by the following facts:

- Metals are chelated or complexed by ligands that are compatible in petroleum (separation is made difficult).
- The amount of metals usually ranges from 1 to 100,000 ppb (these small amounts also make separation difficult).
- Metals are associated with the heterocyclic organic molecules and the asphaltic fraction.
- Metals removal may enhance petroleum refining catalyst life, but their removal may alter the reaction path from a more favored one when the metals are present.

In order to explain the common belief that porphyrin metal complexes in petroleum had their origin from chlorophylls, some process must exist by which the magnesium in chlorophyll is removed and then replaced by other metal ions such as Ni^{+2} and VO^{+2}. The reaction to describe this process can be generalized as follows:(39)

$$2H^{+} + \text{metal porphyrin} \rightleftarrows \text{porphyrin}\cdot 2H + \text{metal}^{+2} \quad .$$

The forward reaction, which is demetallization, produces the porphyrin·2H base and the metal ion by reacting with an acid. The reverse reaction, of course, is metallization. The strength of acid systems required to promote the demetallization reaction is also a measure of the chemical stability of the porphyrins. The following generalizations on their stability were presented by Yen(139):

Acid System	Metal Ions Removed From Porphyrin Complexes
Water	Ag(I), K(I), Na(I), Pb(II), Hg(II)
Dil HCl	Zn(II), Cd(II), Mg(II), Fe(II)
Conc H_2SO_4	Cu(II), Mn(II), Co(II), Ni(II), Fe(III)
HBr-acetic acid	VO(IV)
Trichloroacetic acid	VO(IV)

The best method for demetallization has been the acid treatment. Glacial acetic acid-HBr is a traditional method (The Groenning Process). Methansulfonic acid, p-toluene sulfonic acid, sulfuric acid, and phosphoric acid all can be used for demetallization of porphyrins. Unsuccessful methods cited by Yen include the use of ion exchange, electron discharge, and dialysis.(139)

Erdman and Harju(151) have shown that asphaltenes are undersaturated with respect to metal ions and that sites in sheets are available for holding metal ions by complexing. This was demonstrated by the observed takeup of vanadium, nickel, and copper ions from aqueous solutions by asphaltenes. Similar behavior would be expected for Fe, Zn, Co, Cr, and Hg. Gulyaeva and Lositskaya(152) found that uptake of vanadium occurred only when asphaltenes were present in the crude oil and that it was inhibited by high concentrations of NaCl and in solutions with pH >7. Filby substantiated such behavior by observing the uptake of copper from solutions by asphaltenes.(143)

Hydrodesulfurization of petroleum not only depolymerizes some asphaltenes but a porportional removal of metal is also observed.(139,153,154) It has been demonstrated that when aryl or alkyl derivatives of Sb, Bi, Sn, and As are hydrogenated, the products are the metal and the saturated hydrocarbon with no apparent side reactions. Similar behavior was observed for the cyclopentadiene π-complexes of nickel and iron (ferrocene-type compounds).(155)

Characteristics of Trace-Nonmetal Contaminants in Petroleum. Of the trace elements of interest in this study, As, Se, Te, P, F, Cl, and Br have been categorized as nonmetals. No values for the concentration of phosphorus or tellurium in petroleum were found; therefore, their compounds could not be characterized. Arsenic has been considered in the previous sections and is assumed to be present partially as readily hydrolyzable compounds and as alkyl or aryl arsines. The concentrations of Se, Cl, Br, and I in petroleum have been cited previously. Citations characterizing the selenium compounds could not be found. Of the halogens, the presence of fluorine in crude oils appears to be questionable since in one case it was found(133) and in another it was not.(134) Chlorine, bromine, and iodine are believed to be present in oils as suspensions of metal salts rather than organic molecules. The behavior of iodine during distillation suggests that it forms, or is present as, volatile compounds that appear to be isolated in the 80-170 C fraction. No report of similar behavior for bromine was noted.(130) During distillation at 200 to 300 C, hydrogen chloride gas, HCl, is evolved; the amount is dependent on the chlorine content but was found to increase with increasing nitrogen content. This suggested to the authors that organic nitrogen complexes of $NiCl_2$ were the source of the correlation.(156)

Correlation in the occurrence of the halogens with other trace elements suggests their mode of occurrence but does not truly characterize the nature of their compounds. It has been determined that the bromine concentration generally follows the nickel and vanadium concentrations but not always, and it even varies in different parts of the oil field.(157) The same authors showed that the chlorine concentration is related to the concentration of Na, K, Al, and Mn and suggest that chloride salts are the source of chlorine in petroleum. In a comparison of the concentrations of 25 elements in petroleum with those found in living organisms, bromine was in the group of elements whose concentrations were lower than those in organisms, while iodine was present in concentrations equal to those found in organisms.(158)

2.6.4. Trace Elements in Tar Sand Oils and Shale Oils

Tar sand oils (or raw bitumen) and shale oils have been characterized primarily for their trace-metal content. Since tar sand oils are considered to be geologically younger petroleum, intercomparisons of their trace-metal content have been made. Also, since a major portion of the metal contaminant in petroleum can be located in the resin and asphaltene component of petroleum, a comparison of the resin and asphaltene content of tar sand oils should give some measure of the amounts of trace metals that would be expected in each of the liquid fuels. The amounts of resin and asphaltene isolated from tar sand oils, shale-oil fractions, and two coal liquids have been reported, and the results are summarized in Table 58.(15) The component separation was done by the procedure developed for the study and is similar to those employed in the petroleum trace-metal characterization studies.(143)

TABLE 58. RESINS AND ASPHALTENE CONTENT OF TAR SAND OILS, SHALE OIL FRACTIONS, AND COAL LIQUIDS(15)

Isolated Component	Content, weight percent					
		Coal Liquids		B.P. of Shale Oil Cuts		
	Tar Sand Oils	Big Horn Coal	Pitt Seam Coal	60-282 C	282-360 C	> 360 C
Resin (nonhydrocarbons)	25.9	8.3	11.1	12.1	38.6	68.6
Asphaltene	9.8	1.5	20.3	0.7	0.8	3.3
Benzene insoluble	< 0.1	< 0.1	5.5	< 0.1	< 0.1	< 0.1

The data in Table 58 show that the tar sand oils are very high in resins and asphaltenes. The asphaltene content in shale oil varies with the boiling range of the shale-oil fractions from very low to that comparable to the content in some crude oils (< 5 percent). The resin content ranges from less than that present in crude oils (~35 percent) to almost twice as much. These facts, along with the data on trace-metal characterization reported earlier, suggest that the trace metals in tar sand oils and shale oils exist in the same form as they do in petroleum.

A comparison of the nickel and vanadium in known asphaltic oils, given in Table 59, supports this relationship between petroleum and tar sand oils (Athabasca).(159) The similarity in the excess of vanadium and nickel to porphyrin content also suggests similarities in the types of trace-element compounds that are present in petroleum. The nickel and vanadium concentrations appear to be independent of ash content of the recovered tar sand oils.(136) However, the metals and their concentrations will depend on the characteristics of host rocks. For example, Athabasca tar sand oil contains anomalously high concentrations of Mo, Dy, and Eu which may be related to the presence of minerals such as molybdenite in the sand.(143) The molybdenum concentration in several oils and tar sand oils has been found to range from less than 0.4 ppm (the detection limit of the analytical method) up to 10 ppm.(160) Thirty-five percent was found in the heptane-soluble fraction of the tar sand oil and 42 percent in the insoluble fraction (77 percent accountability). Iron and copper have also been found at concentrations of 75 and 5 ppm, respectively.(12,137) Vanadyl and nickel porphyrins have been isolated from various other tar sand oils and solid hydrocarbons such as those from Utah and California deposits. In Utah, the oils contain more nickel than vanadium.(148) Virtually all of the metals remain in the coke from the delayed-coking operations used to recover the volatile portions from raw bitumen (tar sand oil).(122)

With respect to the volatile shale-oil fractions, the small amount of asphaltenes is not surprising and larger fractions would not be expected since they are products of retorting.(15) Regardless of this fact, crude shale oils contain 4 to 6 ppm nickel, 1.5 to 6 ppm vanadium, and 55 to 100 ppm iron.(19) All oil shales contain porphyrins principally as metal complexes

TABLE 59. PORPHYRIN AND TRACE-METAL CONTENTS OF CERTAIN ASPHALTIC OILS(159)

	Tatums	Athabasca[a]	S.M. Valley	N. Belrdige	Colesville
Vanadium, ppm	110	180	280	23	94
Nickel, ppm	55	80	130	83	32
$\frac{\text{Vanadium}}{\text{Nickel}}$, mole ratio	2.3	2.6	2.5	0.3	3.4
Porphyrin aggregate, ppm	165	260	300	390	110
$\frac{\text{Total V + Ni}}{\text{Total Porphyrin}}$, mole ratio	9.1	9.0	12.2	2.3	10.4

(a) Tar sand oil

with vanadyl and nickel cations, with some iron porphyrin being present as well. The retorted oil contains alkyl porphyrins of the etio series. Since such complexes are stable, some survive the retorting and codistill with the oil products and organic nitrogen derivatives.(148) Iron compounds other than pyrites are closely associated with the kerogen (organic) in the oil shale.(125)

Quantitative determinations have shown that arsenic is present at a 40-ppm concentration in crude shale oil.(138) In addition to arsenic, the following trace elements have been found in shale oil: Sb, Be, B, Cd, Ca, Cr, Co, Cu, F, Ge, Pb, Mg, Mn, Hg, Mo, K, Se, Ag, Na, Sr, Te, Ti, V, Y, and Zn. These trace elements are dissolved in various forms in the oil and differ from the form of the fine suspended solids entrained during oil pyrolysis. Their origin, however, may have been closely related to the mineral matter. The trace elements can be concentrated in the heavy end. Arsenic, however, is distributed throughout the boiling range(138) (probably as various organo-arsine derivatives, as shown below.(143)

Boiling Range, C	Fraction, volume percent	Arsenic Content, ppm
IBP-204	18	10
204-482	58	52
482+	24	38

The nature of the compounds of the other trace elements dissolved in shale oil has not been defined.

3. CONCLUSIONS

The detailed characterization of the sources of sulfur, nitrogen, and trace element contaminants in fuels, such as coal, coal liquids, petroleum, shale oil, and tar sand oil, can best be done with an understanding of the characteristics of and the differences in these fuels. As shown in Table 60, typical fuel types considered in this review exhibit marked differences in the amount of ash forming matter they contain and in the elemental composition of their combustible part. Coals have a much higher ash content than do petroleum crudes. Coals also have the lowest value for the H/C ratio and are considered in a state of unsaturation with respect to hydrogen. To approach petroleum crude in character, hydrogen must be added to coals or coal liquids (obtained by coal pyrolysis). The ratio for shale oil and tar sand oil fall between coal and petroleum. Formation of coal liquids by hydrogenation of coal increases the H/C ratio. Such processes also significantly reduce the amount of sulfur and nitrogen remaining in the fuel.

The review of the characteristics of the components of coal, petroleum, tar sand oil, and shale oil which are the sources of sulfur, nitrogen, and trace element pollutants when these fuels are utilized suggests that at least part of the sulfur and most of the nitrogen originate from compounds common to all of these fuels. These compounds are primarily organic sulfur and nitrogen compounds. The principal difference between the solid and liquid fuels is the way in which these compounds are combined in the fuel. The noncombustible matter associated with coal distinguishes it from the liquid fuels and is the source of inorganic sulfur and most of the trace elements. In liquid fuels the trace elements are present primarily as oil soluble compounds or associated with the colloidal suspensions commonly present in them.

3.1. Contaminants in Solid Fuels

In coal, the nitrogen contaminants are present primarily as organic compounds which are part of the three-dimensional carbon skeletal

TABLE 60. ELEMENTAL ANALYSIS OF TYPICAL FUELS

	Weight Percent						H/C (Atomic)
	C	H	O	N	S	Ash	
Coal (mf)							
Subbituminous (Big Horn)	69.2	4.7	17.8	1.2	0.7	6.5	0.81
Bituminous (Pittsburgh)	78.7	5.0	6.3	1.6	1.7	6.9	0.76
Coal Liquids (Big Horn)	89.2	8.9	1.03	0.4	0.04	>1	1.20
(Pittsburgh)	89.1	8.2	1.5	0.8	0.2	>1	1.10
Shale Oil	80.3	10.4	5.9	2.3	1.1		1.55
Utah Asphalt	82	11	3	2	2		1.61
Petroleum Crude (Pennsylvania)	85	14	1	1	1	<1	1.98

structure that makes up the organic matter of coal. Indirect evidence suggests that the nitrogen compounds exist as both alkyl and aryl derivatives of amines, quinolines, and carbazoles. The sulfur in coal is present both as organic and inorganic compounds. The organic sulfur compounds are also part of the carbon skeleton of coal and consist of both alkyl and aryl derivatives of thiols, thioether, disulfides, and thiophene. The major sources of inorganic sulfur in coal are the pyrites and the sulfate salts. Neither of these sources are part of the organic portion of coal. Pyrites and other mineral matter exist in raw coal as discrete phases ranging in size from gross inclusions in the coal seam to micron-size particles disseminated throughout the organic matter of coal. Trace elements that exist in raw coal can be categorized into those found principally with the organic matter of coal and those present principally in the mineral matter associated with coal. However, there are some trace elements that exhibit a dual role and are found in both components. Trace metals and metalloids exist as complexes of the organic oxygen, nitrogen, and sulfur compounds or as crystal-lattice impurities in the mineral matter associated with coal seams. Nonmetallic trace elements are found primarily as part of the inorganic mineral impurities. Some, such as phosphorus, are found also in the organic part of coal.

It can be concluded that nonuniform distribution of impurities exists not only from one coal seam to another but also within the coal seam. Despite this limitation, intrinsic centers of sulfur and nitrogen contamination have been identified. The organic sulfur and nitrogen compounds are uniformly distributed in the organic part of the coal, as are the trace elements associated with it. Inorganic sulfur and the trace elements associated with the mineral matter in the coal are considered to be variable with the source of coal. However, with the use of modern mining and coal-preparation techniques, a more uniform product is available for use.

3.2. Contaminants in Liquid Fuels

In petroleum and tar sand oil, and to some extent in shale oil, the majority of the organic sulfur and nitrogen compounds found in the asphaltene and resin fractions are similar to those found in coal. In petroleum nearly 50 percent of these fractions consist of molecules in the 4,000 to 8,000 molecular-weight range. Between 10 and 50 percent of the nitrogen and 3 and 35 percent of the sulfur in petroleum are found in these fractions. Similar distributions are indicated for tar sand oils. However, shale oil, because it is formed by thermal degradation of the kerogen in oil shale during retorting, contains much less asphaltenes than either petroleum or tar sand oil. As a result, the organic sulfur and nitrogen contaminants are found mostly in the resin fraction of shale oil. Although coal liquids are known to contain resin and asphaltene fractions, the liquefaction process by the addition of hydrogen to coal also reduces the sulfur content (and at times the nitrogen content) to low levels. The contaminants in coal liquids remaining after removal of the solids are present as organic sulfur and nitrogen compounds that are difficult to remove and are usually found in the higher molecular-weight asphaltene and resin fractions of coal liquids.

It can be concluded that in the liquid fuels, the intrinsic centers of sulfur and nitrogen contamination are found in the colloidal suspensions, otherwise known as asphaltenes, and in the more soluble resins, both of which make up anywhere from 1 to 43 percent (but more commonly less than 6 percent) of the petroleum, about 37 percent of tar sand oils that have been characterized, 13 to 71 percent of the shale oil, and 10 to 30 percent of the coal liquids. However, the molecular weights of the asphaltenes and resins in petroleum crudes are greater than those in synthetic crudes, as shown in Tables 6 and 53. Trace elements in petroleum, tar sand oil, and shale oil are present as oil soluble compounds (usually as porphyrin or porphyrin-like complexes) and adducts to molecules making up the resins and asphaltene fractions. Alkyl and aryl derivatives of the metal or metalloid elements that do not exist as complexes or salts of organic acids make up the other group of oil soluble compounds. Nonmetallic trace elements such as chlorine and bromine are present usually as suspension materials in the oil.

3.3. Distribution of Contaminants in Fuels

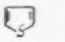
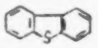
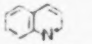
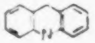
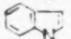
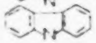
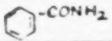
3.3.1. Sulfur and Nitrogen Contaminants

The distribution of sulfur and nitrogen contaminants in the fuel types is shown in Table 61. Large variations in the total sulfur and nitrogen content exist between the fuels and within a fuel type. Coal is unique with respect to the other fuels in that sulfur is also present in the form of pyrites. The organic sources of sulfur in coal have been determined indirectly primarily from studies on depolymerized coal. The exact nature of organic sulfur in solid coal can only be surmised from these studies. There is strong evidence that mercaptans, sulfides, and disulfides are present in the coal structure. The same type of compounds are usually present in tar sand oils and petroleum but not in coal liquids and shale oils. Thiophenes and benzothiophenes are known to be present in coal liquids and shale oil as well as in tar sand oil and petroleum.

The amount of total nitrogen contained in fuels is the highest in coal and shale oil. Little is known for certain about the types of nitrogen compounds contained in coal. The characterization of the nitrogen compounds in coal has been determined indirectly from studies on coal tars or depolymerized coal. There is good evidence that pyridine, quinoline, acridine, indole, carbazole, and porphyrins or their derivatives acccount for the nitrogen in solid coal. Thus, it may be concluded that the nitrogen in coal is present as aromatic compounds. Quinolines, pyrroles, indoles, carbazoles, acridines, and porphyrins are present in coal liquids, shale oil, tar sand oil, and petroleum. Benzamides have been found in shale oil and petroleum. The porphyrin compounds may contain trace metals as coordination compounds.

Values for the amount of each type of organic sulfur and nitrogen compound are available for only a limited number of fuels and then for only a few sources of the fuel type (e.g., petroleum). Others have not yet been characterized or are in the process of being characterized (e.g., coal liquids, shale oils, and tar sand oils). Until additional data are made available, a quantitative comparison would be difficult. But it has been

TABLE 61. DISTRIBUTION OF S AND N CONTAMINANTS IN FUELS

Contaminants		Fuel				
Type and Source	Parent Structure	Coal	Coal Liquids Primary	Shale Oil[(a)]	Tar Sand Oil[(b)]	Petroleum Crude
Sulfur, Total		0.4-13%	<1%	1.1%	0.2-6.3%	0.1-5%
Inorganic						
Pyrites	FeS_2	X[(c,d)]				
Organic						
Mercaptans	R-SH[(e)]	X[(f)]			X	X
Sulfides	R-S-R[(e)]	X[(f)]			X	X
Thiophenes		X[(f)]	X	X	X	X
Benzothiophenes		X[(f)]	X	X	X	X
Nitrogen, Total		1-2.1%	>1%	2.3%	<1%	<<1%
Basic						
Pyridines		X[(f)]	X			
Quinolines		X[(f)]	X	X	X	X
Acridines		X[(f)]	X			X
Nonbasic						
Pyrroles		X[(f)]	X	X	X	X
Indoles		X[(f)]	X	X	X	X
Carbazoles		X[(f)]	X	X	X	X
Benzamides		X[(c,f)]	X	X	X	X

(a) Colorado shale oil.
(b) Tar sands including Utah tar sands.
(c) 48 percent of total sulfur, a mean value for U.S. coals.
(d) Represents the presence of the contaminant in the fuels.
(e) R is an alkyl or aryl group.
(f) Inferred from studies on coal tar, depolymerized coal, and liquefied coal.

determined that the total nitrogen content of U.S. coals (maf) varies in the range of 1 to 1.9 weight percent for lignite and high volatile bituminous coal, respectively. Though this amount of nitrogen appears small, the nitrogen is present as an integral part of the chemical structure of coal.

3.3.2. Trace Elements

The trace elements in the fuels covered in this review can be categorized as to their association either with the organic matter making up the fuel or the mineral matter associated with it. As shown in Table 62, coal, by virtue of its large mineral matter content, has most of the trace elements closely associated with these minerals. Petroleum and tar sand oils by comparison contain much less mineral matter and hence less trace elements associated with them (e.g., those elements commonly associated with brines and suspended sands and clays). Shale oils contain finely divided shale minerals carried over during retorting and contain trace elements found in the shale minerals. In the case of the formation of liquids from coal, the trace elements associated with the mineral matter in coal remain insoluble and are removed along with the mineral matter.

The trace elements more closely associated with the organic matter in coal are shown in Table 63. These trace elements in coal are held in the organic matrix as complexes of organic compounds (containing oxygen, sulfur, or nitrogen), porphyrins or amino acids, or as alkyl- or aryl-derivatives. Most of the trace metals found in petroleum and tar sand oils are found in the organic phase as oil soluble compounds. They exist primarily as complexes, organic acid salts, and alkyl- and aryl-derivatives. Shale oil also contains a large number of oil soluble trace elements which may have formed during retorting. Coal liquids would be expected to contain in solution those elements most closely associated with the organic part of coal or those that enter into solution during the liquefaction process.

TABLE 62. TRACE ELEMENTS ASSOCIATED WITH MINERAL MATTER IN SOLID AND LIQUID FUELS

Mineral (Percent of Total)	Trace Elements
Coal	
Shales, Kaolins (52)	Si, Al, Ti, K (B, Cu, F, Hg, Sn, V)(a)
Sulfides, Pyrites (25)	Fe, Zn, Cd, Pb, Ni, Cu (Hg, B, As, Be, Sb, Ge)(a)
Carbonates (9)	Ca, Mg, Mn (B, Cd, Mo, Se, V)(a)
Chlorides (0.1)	Na, K, Cl (Br, I, Mg, Ca)(a)
Quartz (1-20)	Si (B, Cr, Mn, Cd, Mo, Ge, Se, V, Zn)(a)
Apatite	Ca, P, F (As, V, Cl, Mn, Ce)(a)
Sulfates	Fe, Ca, (Mn)(a)
Petroleum (Tar Sand Oils)	
Chloride (Trace)	Na, K, Mg, Ca, Cl, Br, I (Mn)(a)
Quartz (Trace)	Si
Shales, Kaolins (Trace)	Si, Al, K
Shale Oils	
Shale Minerals	As, Ba, B, Cu, Cr, Pb, Li, Mo, Mn P, Se, Sr, Tl, Ti, V, Zn, Ag, Au
Coal Liquids (Speculation)	
Removed with Mineral Matter	Hg, Zn, Zr, Cd, As, Pb, Mo, Mn (Co, Ni, Cr, Se, Cu, Sb, V, Ti, Ga, P)(b)

(a) Elements in parentheses are known to have high correlation with minerals but not necessarily detected with minerals.

(b) The elements in parentheses are more commonly found with mineral matter but are also found in organic portion of coal.

TABLE 63. TRACE ELEMENTS ASSOCIATED WITH ORGANIC MATTER OF SOLID AND LIQUID FUELS

Derivative	Trace Elements
Coal	
Complexes of O,N,S Ligands and Organic Acid Salts	Ge, Be, B, Ti, U (Ga, Y, La, Ni, Co, Zn, V, Ca, Al, Si, P)(a)
Porphyrin , Amino Acids	V, Ni, Cu, Fe
Alkyl- or Aryl-	Ge (P, Se)(a)
Petroleum (Tar Sand Oils)	
Porphyrin	Ni, V
Nonporphyrin	Ni, V, Fe, Co, Zn, Hg, Cr, Cu
Tetradentate Complexes (S,N,O)	V, Ni, Fe, Cu, Co, Cr (Cl)(b)
Alkyl- or Aryl-	Hg, Sb, As
Organic Acid Salts	Na, As, Hg, Fe, Sb (Mo)(a)
Unknown	Se, I
Shale Oils	
Oil Soluble	As, Sb, Be, B, Cd, Ca, Cr, Co, Cu, F, Ge, Pb, Mg, Mn, Hg, Mn, Mo K, Se, Na, Sr, Te, Ti, V, Y, Zn
Coal Liquids (Speculation)	
Liquid Soluble (?) > 50 percent Organic Affinity	Ge, Be, Ga, B, Ti (P, U, V, Sb, Co, Ni, Cr, Se, Cu)(c)

(a) Elements forming compounds to a lesser extent are in parentheses.

(b) Cl^- suggested as counter ion.

(c) Elements in parentheses are more closely associated with organic part of coal but are also present in mineral matter.

Of the trace metals known to be present in coal, V, Ni, Ge, Be, B, Ti, Ga, and Sb have been shown to be closely associated with organic part of coal. Of these elements, only Ni, V, B, Ti, Ga, and Sb have been reported in the crude oils for which analyses were given. Table 64 presents a correlation of the trace elements with their organic affinity in coal and with their occurrence in petroleum. Germanium and beryllium (and perhaps phosphorus), which have strong organic affinities in coal, are not reported in many of the world petroleums. Conversely, the number of trace elements found dissolved in petroleum far exceeds those closely associated with the organic part of coal. Arsenic is a good example. In some oils, it is present as oil soluble compounds, some of which are water hydrolyzable, while in coal arsenic exists predominantly with mineral matter (close to zero organic affinity). In shale oil, arsenic is present as an oil soluble and volatile compound. Other metals such as Na, Cu, Co, Fe, Hg, and Cr follow a similar distribution pattern in petroleum and coal as arsenic does.

3.4. Potential for Removal of Contaminants

3.4.1. Contaminants Present as Discrete Phases

The potential for the removal of contaminants that are present as a discrete phase such as pyrites and other mineral matter in coal or brine in petroleum is technically and economically feasible. In the case of coal, size reduction is needed to free the mineral occlusions. However, since the pyrite in some coals is present in the micron size range, there would appear to be a practical limit in the size that coal can be pulverized to expose the pyrite. Density differences should provide a means for their separation. Similar reasoning might apply to other mineral phases dispersed in the coal. Pyrite might also be removed by selective chemical attack. Separation of brine and water soluble salts from petroleum would require the addition of water and separation of the two phases.

TABLE 64. METAL CONTAMINANTS ASSOCIATED WITH ORGANIC MATTER IN COAL AND COMPARED TO THEIR PRESENCE IN PETROLEUM

	V	Ni	Ge	Be	B	Ti	Ga	Sb
			Coal					
Occurrence in Percent(a) of 13 Coals	100	100	100	100	100	100	100	92
EPA Sample (a) ppm(b)	36	--	70	--	--	1,312	5.4	6.4
(b) ppm	16	--	--	--	--	1,100	--	3.7
101 Samples ppm(c) (mean)	32.7	21.07	6.59	1.61	102.2	700	3.12	1.26
(range)	(11.0-78.0)	(3.0-80.00)	(1.00-43.00)	(0.20-4.00)	(5.00-224.0)	(200-1500)	(1.10-7.50)	(0.20-8.90)
Organic Affinity(d) (percent)	76	59	87	82	77	78	79	--
Association(e)	Org Aff II	Inorg Aff II	Org Aff I	Org Aff I	Org Aff I	Org Aff II	Org Aff II	Org Aff II
			Petroleum					
Occurrence in Percent(f) of 24 Crudes	100	100	--	--	17	50	67	--
Range of ppm(g) (4 Samples)	0.7-1100	0.7-117	Not Reported	Not Reported	Not Reported	Not Reported	0.01-0.3	0.06-0.303

(a) According to Kessler, Reference 83 and Figure 8.
(b) According to References 85 and 86 and Tables 34 and 35.
(c) According to Ruch, Reference 80 and Table 36.
(d) According to Zubovic, Reference 87 and Table 39.
(e) According to Ruch, Reference 80 and Table 38.
(f) According to Ball, Reference 120 and Table 46.
(g) According to Filby, Reference 128 and Table 48.

3.4.2. Contaminants Present as Part of Fuel Structure

Sulfur, nitrogen, and trace elements that are present in the fuel as part of the organic structure will require severe methods for their selective removal. The potential for their removal from a liquid fuel would be greater than from a solid fuel because of contact problems between a reagent and solid fuel. One alternative might be to remove the molecules containing the sulfur, nitrogen, or trace element by reaction with a reagent and subsequent removal from the fuel. For simple alkyl compounds this would seem practical as the weight of sulfur or nitrogen removed would be comparable to the weight of the original compound. However, for compounds such as dibenzothiophene or carbazole the sulfur and nitrogen contaminant is only 17 and 8 percent, respectively, of the compound weight and the associated fuel carbon losses would not make the approach practical. Such an approach would first require the conversion of coal to a liquid either by hydrogenation or pyrolysis. Another alternative might be to disrupt the molecular structure of the molecules containing the sulfur and/or nitrogen by (1) hydrogenation to release the sulfur and nitrogen as H_2S or NH_3, (2) selective chemical attach and subsequent liberation of the contaminant, or (3) partial oxidation and gasification followed by gas purification. Such approaches would appear to be suited for both solid and liquid fuels.

The choice of the approach to remove sulfur and nitrogen contained in organic compounds from solid or liquid fuels would thus depend on whether the desired clean final product is to be a liquid or a gas. Removal of these same impurities to yield a clean solid fuel would be highly desirable yet appears to be difficult to accomplish.

4. REFERENCES

4.1. Fuel and Fuel Contaminant Characterization

(1) Carman, E. P., and Bayes, F. S., "Occurrence, Properties, and Uses of Some Natural Bitumens", U.S. Bureau of Mines IC 7997 (1961).

(2) Lowry, H. H., "Chemical Constitution and Reactions in Coal", Chemistry of Coal Utilization, John Wiley and Sons, New York (1963).

(3) Walker, P. L., "Coal Characteristics and Gasification Behavior", Coal Short Course, Pennsylvania State University (November, 1973).

(4) Chakrabaty, S. K., and Berkowitz, N., "Studies on the Structure of Coals, 3. Some Inferences About Skeletal Structure", Fuel 53, p 240 (1974).

(5) Cartz, L., and Hirsch, P. B., "A Contribution to the Structure of Coals from X-Ray Diffraction Studies", Phil. Trans. Roy. Soc., 252A, p 557 (1960).

(6) Given, P. H., "The Distribution of Hydrogen in Coal and Its Relation to Coal Structure", Fuel, 39, p 147 (1960).

(7) Wiser, W. H., "Some Chemical Aspects of the Conversion of Coal to Liquids and Gaseous Fuels", EPRI Conference on Coal Catalysis (September 24-25, 1973).

(8) Wender, Irving, "Catalytic Synthesis of Chemicals from Coal", Am. Chem. Soc., Div. of Fuel Chem. Preprint, 20 (4), p 16 (1975).

(9) Tingey, G. L., and Morrey, J. R. "Coal Structure and Reactivity", Battelle Energy Program Report, Battelle Northwest Lab., Richland, Washington (1973).

(10) Smith, M. L., and Stinson, K. W., Fuels and Combustion, McGraw-Hill Book Company, New York (1952).

(11) Kirk-Othmer, Encyclopedia of Chemical Technology, Second Edition, Vol. 14, pp 852-855 (1967).

(12) Camp, F. W., "Tar Sands", in Kirk-Othmer, Encyclopedia of Chemical Technology, Second Edition, Vol. 19, p 682 (1967).

(13) Speight, J. B., "A Structural Investigation of the Constituents of Athabasca Bitumen by p.m.r. Spectroscopy, Fuel, 49 (2), p 134 (1970).

(14) Speight, J. G. "Structural Analysis of Athabasca Asphaltenes by p.m.r. Spectroscopy", Fuel, 50 (2) p 102 (1971).

(15) Ruberto, R. G., et al., "Characterization of Synthetic Liquid Fuels, Am. Chem. Soc., Div. of Fuel Chem. Preprint, 19 (2), p 258 (1974).

(16) Prien, C. H., "Current Status of U.S. Oil Shale Technology", Ind. Eng. Chem. 56 (9), p 32 (1964).

(17) McKee, R. H., et al., Shale Oil, Am. Chem. Soc. Monograph Series (1925).

(18) Schmidt-Collems, J. J., and Prien, C. H., "Investigations of the Structure of Kerogen from Oil Shale of the Green River Formation", Am. Chem. Soc., Div. of Fuel Chem. Preprint, 19 (2), p 100 (1974).

(19) Hendrickson, Thomas A., Synthetic Fuels Data Handbook, Cameron Engineers Inc. (1975).

(20) Yen, T. F., "A New Structure Model of Oil Shale Kerogen", Am. Chem. Soc., Div. of Fuel Chem. Preprint, 19 (2), p 109 (1974).

(21) Given, P. H., and Wyss, W. F., "The Chemistry of Sulfur in Coal", The British Coal Utilization Research Association Bull., XXV (5), p 165 (1961).

(22) Anderson, H. C., and Wu, W. R. K., "Properties of Compounds in Coal Carbonization Products", U.S. Bureau of Mines, Bull. 606 (1963).

(23) Walker, F. E., and Harner, F. E., "Forms of Sulfur in U.S. Coals", U.S. Bureau of Mines IC 8301 (1965).

(24) Staff, Office of the Director of Coal Research, "Methods of Analyzing and Testing Coal and Coke", U.S. Bureau of Mines, Bull. 638 (1967).

(25) Headlee, A. J. W., and Haskins, H. A., "Sulfur in Coals", Characteristics of Minable Coals of West Virginia, West Virginia Geological Survey, Vol. 13 A (1955).

(26) Gluskoter, H. J., "Inorganic Sulfur in Coal", Am. Chem. Soc., Div. of Fuel Chem. Preprint, 20 (2), p 94 (1975).

(27) Yancey, H. F., and Fraser, T. "Coal Washing Investigations: Methods and Tests", U.S. Bureau of Mines, Bull. 300 (1929).

(28) Yancey, H. F., and Greer, M. R., "Properties of Coal and Impurities in Relation to Preparation", in Coal Preparation, J. W. Leonard and D. R. Mitchel, Editors, AIME, New York, pp 1-45 (1968).

(29) Hamilton, P. A., White, D. H., Jr., and Matson, T. K., "The Reserve Base of U.S. Coals by Sulfur Content: Part 2 Western States", U.S. Bureau of Mines, IC 8693 (1975).

(30) Thomson, R. D. and York, H. F., "The Reserve Base of U.S. Coals by Sulfur Content: Part 1 Eastern States", U.S. Bureau of Mines, IC 8680 (1975).

(31) Friedmann, S. Yavorsky, P. M., and Aktar, S., "The Synthoil Process", Clean Fuels from Coal II, Proceedings, I.G.T. (June 23-27, 1975).

(32) Anderson, R. P., and Wright, C. H., "Coal Desulfurization in the P & M Solvent Refining Process", Am. Chem. Soc., Div. of Fuel Chem. Preprint, 20 (1), p 2 (1975).

(33) Aktar, S., Sharkey, A. G. Shultz, J. and Yavorsky, P. M., "Organic Sulfur Compounds in Coal Hydrogenation Products", Am. Chem. Soc., Div. of Fuel Chem. Paper 22, 167th ACS Meeting (1974).

(34) Harthongh, H. D., "Chemistry of Sulfur Compounds in Petroleum", Adv. in Pet. Chem. Ref., Vol. 111, p 419, Interscience Publishing Co., New York (1960).

(35) Rall, H. T., et al., "Sulfur Compounds in Crude Oils", U.S. Bureau of Mines Bull. 659 (1972).

(36) Jewell, D. M., et al., "Distribution and Structural Aspects of Sulfur Compounds in Residuals", Am. Chem. Soc., Div. of Pet. Chem. Preprint, 20 (4), p. 743 (1975).

(37) "Energy from U.S. and Canadian Tar Sands: Technical Environmental, Economic, Legislative, and Policy Aspects", Report prepared for the Subcommittee on Energy of the Committee on Science and Astronautics, U.S. House of Representatives, 93rd Congress (December, 1974).

(38) Clugston, D. M., et al., "Sulfur Compounds in Oils from the Western Canada Tar Belt", Am. Chem. Soc., Div. of Fuel Chem. Preprint, 19 (2), p 202 (1974).

(39) Dineen, G. U., "Sulfur and Nitrogen Compounds in Shale Oil", Proc. Amer. Petrol. Inst., 42 (VIII), p 41 (1962).

(40) Sohns, H. W., et al., "Development and Operation of an Experimental Entrained Solids, Oil-Shale Report", U.S. Bureau of Mines RI 5522 (1959).

(41) Stanfield, K. W., et al., "Properties of Colorado Oil Shale", U.S. Bureau of Mines RI 4825 (1951).

(42) Price, C. C., and Oae, S., Sulfur Bonding, Ronald Press Company, New York (1962).

(43) Reid, E. E., Organic Chemistry of Bivalent Sulfur, Vols. 1, 2, and 3, Chemical Published Company, New York (1958, 1960).

(44) Hartough, H. D., Thiophene and Derivatives, Interscience Publishers, Inc., New York (1952).

(45) Hauck, R. D., "The Genesis and Stability of Nitrogen in Peat and Coal", Am. Chem. Soc., Div. of Fuel Chem. Preprint, 20 (2), p 85 (1975).

(46) Birkofer, Von L., and Orywal, F., "Beitrag zur kenntris der Bindugsarten des Stickstoffs in Steinkohle", Brennstoff-Chemie, 48 (8), p 225 (1967).

(47) Imuta, K., and Ouchi, K., "Some Compounds Separated from Depolymerization of Brown Coal", Fuel, 52 (7), p 174 (1973).

(48) Beet, A. E., "A Further Study of the Kjeldal Process: Pyridene Carboxylic Acids from Coal", Fuel, 19, p 8 (1940).

(49) Kreuelen Van, D. W., "Functional Group Analysis of Nitrogens", Coal, Elsevier Publishing Company, New York, p 170 (1961).

(50) Parks, B. C., and O'Donnell, H. J., "Petrography of American Coals", U.S. Bureau of Mines Bull. 550 (1957).

(51) Kirner, W. R., "The Occurrence of Nitrogen in Coal", Chemistry of Coal Utilization, John Wiley & Sons, New York (1945).

(52) Shultz, J. L., et al., "High-Resolution Mass Spectrometric Investigation of Heteroatom Species in Coal Carbonization Products", Fuel, 51 (7), p 242 (1972).

(53) Friedel, R. A., Spectrometry of Fuels, Plenum Press, New York (1970).

(54) Ball, J. S., "Nitrogen Compounds in Petroleum", Proceedings Am. Pet. Inst., 42 (8), 27 (1962).

(55) Smith, H., "Crude Oil: Qualitative and Quantitative Aspects", U.S. Bureau of Mines IC 8286 (1966).

(56) Jewel, D. M., et al., "Basic Nitrogen Compounds in Petroleum, Hydrocarbon Analysis", ASTM STP 389, Am. Soc. Testing Mats., 363 (1965).

(57) Latham, D. R., et al., "Nonbasic Nitrogen Compounds in Petroleum, Hydrocarbon Analysis", ASTM STP 389, Am. Soc. Testing Mats., 385 (1965).

(58) Bunger, J. W., "Characterization of a Utah Tar Sand Bitumen", Am. Chem. Soc., Div. of Fuel Chem. Preprint, 19 (2), p 231 (1974).

(59) Cook, G. L., "Nitrogen Compounds in Colorado Shale Oils", Am. Chem. Soc., Div. of Pet. Chem. Preprint, 10 (2), p C-35 (1965).

(60) Poulson, R. E., "Nitrogen and Sulfur in Raw and Refined Shale Oils", Am. Chem. Soc., Div. of Fuel Chem. Preprint, 20 (2), p 183 (1975).

(61) Dineen, G. V., et al., "Estimation of Types of Nitrogen Compounds in Shale-Oil Gas Oil", Anal. Chem., 30, p 2026 (1958).

(62) Jackson, L. P., and Decora, A. Q., "Thermal Reactions of Shale-Oil Components: Plant Pigments as Probable Precursors of Nitrogenous Compounds in Shale Oil", U.S. Bureau of Mines RI 8018 (1975).

(63) Poulson, R. E., et al., "Nitrogen Bases in a Shale-Oil Light Distillate", Am. Chem. Soc., Div. of Pet. Chem. Preprint, 16 (1) (1971).

(64) Dinneen, G. V., et al., "Composition of Shale Oil Naptha", U.S. Bureau of Mines Bull. 593 (1961).

(65) Silver, H. F., et al., "Denitrofication Reactions in Shale Gas Oil", Am. Chem. Soc., Div. of Pet. Chem. Preprint, 17 (4), p G94 (1972).

(66) Karr, C., et al., "Identification of Distillate Tar Acids and Tar Bases from a Low Temperature Bituminous Coal Tar", U.S. Bureau of Mines Bull. 591 (1961).

(67) Badger, G. M., The Chemistry of Heterocyclic Compounds, Academic Press, New York (1961).

(68) Elderfield, R. C., Heterocyclic Compounds, Vol. 3 and 4, John Wiley & Sons, New York (1952)

(69) Roberts, J. D., and Casserio, M. C., Basic Principles of Organic Chemistry, W. A. Benjamin, Inc., New York (1965).

(70) Ode, W. H., "Coal Analysis and Mineral Matter", in Chemistry of Coal Utilization (H. H. Lowry, Ed.), Suppl. Vol., John Wiley & Sons (1963).

(71) Magee, E. M., Hall, H. J., and Varga, Jr., G. M., "Potential Pollutants in Fossil Fuels", Esso Res. and Eng. Co., Linden, New Jersey, EPA-R2-73-249 (1973) PB 225 039.

(72) Abernathy, R. F., Peterson, M. I., and Gibson, F. H., "Spectrochemical Analyses of Coal Ash for Trace Elements", U.S. Bureau of Mines RI 7281 (1969).

(73) Zubovic, Peter, Sheffy, N. B., and Stadnickenko, T., "Distribution of Minor Elements in Some Coals in Various Regions and Coal Provinces in United States", U.S. Geological Survey, Bulletin No. 1117-D, Western and Southwestern of the Interior Coal Provinces (1967).

(74) Ibid., Bulletin No. 1117-A, Northern Great Plains Provinces (1961).

(75) Ibid., Bulletin No. 1117-B, Eastern Coal Region (1964).

(76) Ibid., Bulletin No. 1117-C, Appalachian Region (1966).

(77) Gluskoter, H. J., "Electronic Low Temperature Ashing of Bituminous Coal", Fuel, 44, p. 285 (1965).

(78) O'Gorman, J. V., and Walker, Jr., P. V., "Mineral Matter and Trace Elements in U.S. Coals", Office of Coal Research, U.S. Dept. of Interior, Research and Development Report No. 61, Interim Report No. 2 (1972).

(79) Ruch, R. R., Gluskoter, H. J., and Shimp, N. F., "Occurrence and Distribution of Potentially Volatile Trace Elements in Coal", Interim Report, Environmental Geology Note, No. 61, Illinois State Geological Survey (April, 1973).

(80) Ruch, R. R., Gluskoter, H. J., and Shimp, N. F., "Occurrence and Distribution of Potentially Volatile Trace Elements in Coal", Final Report, Environmental Geology Note , No. 72, Illinois State Geological Survey (August, 1974).

(81) Headlee, A. J. W., and Hunter R. B., "The Inorganic Elements in the Coals", in Characteristics of Minable West Virginia Coals, West Virginia Geological Survey, Vol. XIII A, Morgantown, West Virginia (1955).

(82) Sprunk, G. C., and O'Donnell, H. J., "Mineral Matter in Coal", U.S. Bureau of Mines Tech. Publ. 648 (1942).

(83) Kessler, T., Sharkey, Jr., A. G., and Friedel, R. A., "Analysis of Trace Elements in Coal by Spark-Source Mass Spectrometry", U.S. Bureau of Mines RI 7714 (1973).

(84) Block, C., and Dams, R., "Determination of Trace Elements in Coal by Instrumental Neutron Activation Analysis", Anal. Chem. Acta. 68, p 11 (1974).

(85) Sheibley, D. W., "Trace Elements by Instrumental Neutron Activation Analysis for Pollution Monitoring", in Trace Elements in Fuel, S. P. Babu, Ed., Adv. Chem. Series, No. 141, American Chemical Society, Washington, D.C. (1975).

(86) Abel, K. H., and Rancetelli, R. A., "Major, Minor, and Trace Element Composition of Coal and Fly Ash as Determined by Instrumental Neutron Activation Analysis", in Trace Elements in Fuels, S. P. Babu, Ed., Adv. Chem. Series 141, American Chemical Society, Washington, D. C. (1975).

(87) Zubovic, P., "Physiocochemical Properties of Certain Elements As Controlling Factors in Their Distribution in Coal", in Coal Science, R. F. Gould, Editor, Advances in Chemistry Series No. 55, American Chemical Society, Washington, D.C. (1966).

(88) Gluskoter, H. J., "Mineral Matter and Trace Elements in Coal", in Trace Elements in Fuels, S. P. Babu, Ed., Adv. Chem. Series No. 141, American Chemical Society, Washington, D.C. (1975).

(89) Poulson, L. B., Beckering, W., and Fawkes, W. W., "Separation and Identification of Minerals from Northern Great Plains Province Lignite", Fuel, 51, p 224 (1972).

(90) Rao, C. P., and Gluskoter, H. J., "Occurrence and Distribution of Minerals in Illinois Coals", Illinois State Geol. Serv. Circ. 476, p 53 (1973).

(91) Estep, P. A., Kovach, J. J., and Karr, Jr., C., Am. Chem. Soc., Div. of Fuel Chem. Preprint, 12 (4), p 1 (1968).

(92) Yancey, and Greer, M. R., "Properties of Coal and Impurities in Relation to Preparation", in Coal Preparation, J. W. Leonard and D. R. Mitchell, Editors, Am. Inst. Mining, Metallurgical and Petroleum Engineers Inc., New York, p I-40 (1968).

(93) Headlee, A. J. W., and Hunter, R. G., "Germanium in Coals of West Virginia", Report of Investigation No. 8, West Virginia Geological Survey, Morgantown, W. Va. (1951). CA 46, 2264 a (1952).

(94) Breger, I. A., Deul, M., and Rubinstein, S., "Geochemistry and Minerology of Uraniferous Lignite", Economic Geology, 50 (2), p 201 (1955).

(95) Corey, R. C., et al., "Occurrence and Determination of Germanium in Coal Ash from Power Plants", U.S. Bureau of Mines Bull. 575 (1959).

(96) Winnicki, J., "Germanium and Inorganic Mineral Matter in Coal of Seam 510 in Upper Selesion Coalfield", Prace Glownego Inst. Gornictwa, Komun No. 352-360, p 159 (1964); CA 62, 11570 c (1965).

(97) Bucklen, O. B., Cockrell, C. F., and Donahue, B. A., et al., "Coal-Associated Minerals of the United States, Part 7 - Uses, Specifications, and Processes Related to Coal Associated Minerals", Office of Coal Research, Contract No. 14-01-0001-269 (PB. 168-116) (1965).

(98) Manskaya, S. M., Drozdova, T. V., and Kravtsova, R. P., "Forms of Compounds of Germanium with Organic Substances of Coals", Geokhimiya 1965 (2), p 188; CA 62, 11570 f (1965).

(99) Bekyorova, E. E., and Rouschev, D. D., "Forms of Germanium in Solid Fuels", Fuel, 50 (3), p 272 (1971).

(100) Ely, F. G., and Barnhart, D. H., "Coal Ash - Its Effect on Boiler Availability", in Chemistry of Coal Utilization, Suppl. Vol., H. H. Lowry, Ed., John Wiley and Sons, Inc., New York, p 841 (1963).

(101) Crossley, H. E., "External Boiler Deposits", J. Inst., Fuel, 25, p 221 (1952).

(102) Crossley, H. E., "Manner of Occurrence of Fluorine in Coal", J. Soc. Chem. Ind. 63, p 289 (1944).

(103) Abernathey, R. F., and Gibson, F. H., "Methods for Determination of Fluorine in Coal", U.S. Bureau of Mines RI 7054 (1967).

(104) Durie, R. A., and Schafer, H. N., "Inorganic Constituents in Australian Coals, IV - Phosphorus and Fluorine - Their Probably Mode of Occurrence", Fuel, 43, p 31 (1964).

(105) Geer, M. R., Davis, F. T., and Yancey, H. F., "Occurrence of Phosphorus in Washington Coal and Its Removal", Am. Inst. Min. Met. Eng., Technical Publication 1586, p 8 (1943).

(106) Smith G. A., "Phosphorus in Coal: Its Distribution and Modes of Occurrence", J. Chem. Met. Mining Soc., S. Africa, 42, p 102 (1941). CA 36, 3929, 2 (1942).

(107) Gluskoter, H. J., and Rees, O. W., "Chlorine in Coals", Illinois State Geological Survey, Circ. 372 (1964).

(108) DeWaele, A., "The Occurrence of Chlorine in Coal", Analyst 40, p 146 (1915).

(109) Sexton, A. H., and Davidson, W. B., Editors, Fuel and Refractory Materials, Van Nostrand, New York p 382 (1921).

(110) Crossely, H. E., "External Boiler Deposits", J. Inst., Fuel, 25 (145), p 221 (1952).

(111) Whittingham, G., "High Temperature Reactions of Coal Minerals During Combustion", British Coal Util. Res. Assoc., Monthly Bulletin 18 (12), p 581 (1954).

(112) Brame, J. S. S., and King, J. G., Fuel; Solid, Liquid, and Gaseous, E. Arnold, London (1935).

(113) Edgecombe, L. J., "State of Combination of Chlorine in Coal: I - Extraction of Coal with Water", Fuel, 35, p 38 (1956).

(114) Daybell, G. N., and Pringle, W. J. S., "The Mode of Occurrence of Chlorine in Coal", Fuel, 37, p 283 (1958).

(115) Kear, R. W., and Menzies, H. M., "Chlorine in Coal: Its Occurrence and Behavior During Combustion and Carbonization", Brit. Coal Util. Res. Assoc., Monthly Bull. 20 (2), (Review No. 156), p 53 (1956).

(116) Parkes, G. D., Mellor's Modern Inorganic Chemistry, Longmans, Green and Co., London, p 766 (1939).

(117) Block, C., and Dams, R., "Inorganic Composition of Belgian Coals and Coal Ash", Env. Sci. and Tech. 9 (2), p 146 (1975).

(118) Kuhn, J. K., Harfst, W. F., and Shimp, N. F., "X-ray Fluoresence Analysis of Whole Coal", in Trace Elements in Fuel, S. B. Babu, Ed., Adv. Chem. Ser. No. 141, American Chemical Society, Washington, D.C. (1975).

(119) Jones, M. C. K., and Hardy, R. L., "Petroleum Ash Components and Their Effect on Refractiries", Ind. and Eng. Chem. 44 (11), p 2615 (1952).

(120) Ball, J. S., Wenger, W. J., Hyden, H. J., Horr, C. A., and Myers, A. T., "Metal Content of Twenty-Four Petroleums", J. Chem. Eng. Data 5 (4), p 553 (1960).

(121) Bowman, C. W., "Molecular and Interfacial Properties of Athabasca Tar Sands", in Proceedings of the 7th World Petroleum Conference, Vol. 3, Elsevier Publishing Co., Ltd., Essex England, p 583 (1967).

(122) McConville, L. B., "The Athabasca Tar Sands", Mining Engineering 27 (1), p 19 (1975).

(123) Kaminsky, V. P., and Nagy, E., "Athabasca Oil Sands: Recovery Methods", in Fossil Carbon and Mineral Processing, Chem. Eng. Prog. Symposium Series 85, Lyon, L. B., and Selin, C., Editors, Vol. 64, p 104 (1968).

(124) Tisot, P. R., and Murphy, W. I. R., "Physicochemical Properties of Green River Oil Shale", J. Chem. and Eng. Data 5 (4), p 558 (1960).

(125) Thomas, R. D., and Lorenz, P. B., "Use of Centrifugal Separation to Investigate How Kerogen is Bound to Minerals in Oil Shale", U.S. Bureau of Mines RI 7380 (1970).

(126) Shah, K. R., Filby, R. H., and Haller, W. A., "Determination of Trace Elements in Petroleum by Neutron Activation Analysis, Part I", J. Radioanal. Chem. 6, p 185 (1970).

(127) Ibid., Part II, p. 413 (1970).

(128) Filby, R. H., and Shah, K. R., "Neutron Activation Methods for Trace Elements in Crude Oils", in The Role of Trace Metals in Petroleum, T. F. Yen, Ed., Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan (1975).

(129) Bryan, D. E., Lukens, H. R., and Guinn, V. P., "Trace Element Characterization of Crude Oils and Fuel Oils via Instrumental Neutron Activation Analysis", Nucl. Tech. Environ. Pollut. Proc. Symp., p 347 (1970). CA75, 89782 (1971).

(130) Ordogh, M., Belazs, A., Reti, S., and Szabo, E. "Determination of I, Br, and V in Crude Oils", Banyasz. Kohasz. Lapol. Koolaj Foldas 6 (3), p 86 (1973). CA79, 55621 (1973).

(131) Gordon, S. A., Menkovskii, M. A., and Kler, V. R., "The Characteristics of Germanium in Crude Oils and Asphaltites", Khim. I. Teknol Topliv. I. Masel. 9 (12), p 32 (1964). CA62, 7551 h (1965).

(132) Orekhov, U.S., Taliev, S. D., and Poplvako, E. M. et al., "Concentration of Rhenium in Petroleums, Petroleum Bitumins, and Oil Shales", Geokhimiya 9, p 1399 (1974). CA82, 61491A (1975).

(133) Wilson, J., Marczewski, C. Z., and Jones, P., "Determination of Fluorine in Petroleums", J. Inst. Petrol, (London) 59, p 42 (1973). CA79, 94237 p (1973).

(134) Hoffman, E., Gottlieb, K., and Mueller, U., "Examination of Petroleum and Petroleum Products with Respect to Fluroine", Erdoel, Kohle, Erdgas, Petrochem. Brennst.-Chem. 26 (11), p 647 (1973). Ca80, p 147467 t (1974).

(135) Columbo, U., "Trace Metals in Petroleum", Riv. Combust. 18, p 462 (1964).

(136) Soutar, P. S., Mc Colgan, E. C., and Parsons, B. I., "Hydrocracking of Residual Oils and Tars, Part 3: Effect of Mineral Matter on Thermal and Catalytic Hydrocracking of Athabasca Bitumen", Can. Dept. Energy, Mines and Resources, Mines Branch, R-256 (1972).

(137) Fear, J. V. D., and Innes, E. D., "Canada's First Commercial Tar Sand Development" in Reference 119, p 633.

(138) Bruger, E. J., Curtin, D. J., Myers, G. A., and Wunderlich, D. K., "Prerefining of Shale Oil, Am. Chem. Soc., Div. Pet. Chem. Preprint, 20 (4), p 765 (1975).

(139) Yen, T. F., "Chemical Aspects of Metals in Native Petroleum", in Reference 126, p 1.

(140) Eldib, I. A., Dunning, H. N., and Bolen, R. J., "Nature of Colloidal Materials in Petroleum", J. Chem. Eng. Data 5 (4), p 550 (1960).

(141) Nelson, W. L., Petroleum Refinery Engineering, 4th Edition, McGraw-Hill, pp 94, 265, and 280 (1958).

(142) Rhodes, R. E., and Yen, T. F., et al., "Mass Spectrometry of Porphyrins 2. Characterization of Petroporphyrins", J. Am. Chem. Soc. 89, p 3631 (1967).

(143) Filby, R. H., "The Nature of Metals in Petroleum", in The Role of Trace Metals in Petroleum, T. F. Yen, Ed., Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan (1975).

(144) Dunning, H. N., and Rabon, N. A., "Porphyrin Metal Complexes in Petroleum Stocks", Ind. Eng. Chem. 48, 951 (1956).

(145) Helm, R. V., Latham, D. R., Ferrin, C. R., and Ball, J. S., "Distribution of Nitrogen Compounds in Wilmington, Ca. Petroleum", Ind. Eng. Chem., Chem. Eng. Data Series 2, p 95 (1957).

(146) Sugihara, J. M., Branthaver, J. F., Wu, G. Y., and Weatherbee, C., "Research on Metal Compounds in Petroleum: Present and Future", Am. Chem. Soc., Div. Pet. Chem. Preprint, 15 (2), p C-5 (1970).

(147) Tynan, E. C., and Yen, T. F., "ESR Study of Vanadium Occuring in Petroleum Asphaltenes in Solution", Am. Chem. Soc., Div. of Pet. Chem. Preprint, 12 (2), p A-89 (1967).

(148) Hodgson, G. W., Baker, B. L., and Peake, E., "The Role of Porphyrins in Geochemistry of Petroleum", Seventh World Petroleum Conference, Vol. 9 p 117, Elsevier Pub. Co. Ltd. (1967).

(149) Dwiggins, Jr., C. W., Willcox, K. W., Doughty, D. A., and Heemstra, R. J., "Separation and Characterization of Metallo-Organic Materials in Petroleum" U.S. Bureau of Mines RI 7273 (1969).

(150) Yen, T. F., "Vanadium and Its Bonding", in Reference 126, p 167.

(151) Erdman, J. G., and Harju, P. H., "Capacity of Petroleum Asphaltenes to Complex Heavy Metals", J. Chem. and Eng. Data 8 (2), p 252 (1963).

(152) Gulyaeva, L. A., and Lositskava, I. F., "Reactions of Oils with Vanadium in Aqueous Solution", Geochemistry International (Eng. Trans.) 1967 (7), p 699.

(153) Ebel, R. H., "Recent Advances in Fuel Desulfurization Technology", Am. Chem. Socl, Div. of Pet. Chem. Preprint, 17 (3), p C-46 (1972).

(154) Drushel, H. V., "Analytical Characterization of Residual and Hydrotreated Products", Am. Chem. Soc., Div. of Pet. Chem. Preprint, 17 (4), p F-92 (1972).

(155) Thompson, C. J., et al., "Characterization of Non-hydrocarbon Constituents of Petroleum by Microhydrogenation", in Reference 146, p 93.

(156) Sapiro, M. D., Stomenko, A. E., and Kulik, A. P., "Determination of Chlorine in Petroleum", Neft. Gazov Prom, 1973 (6), p 30. CA81, 15291 s (1974).

(157) Al-Shahristani, H., and Al-Attiya, M. J., "Trace Elements in Iragi Oils and Their Relationship to the Origin and Migration of These Oils", CA81, 108149 s (1974).

(158) Gulyaeva, L. A., and Rumanova, S. A., "Petroleum Trace Elements, Relics of Living Matter", Izv. Akad, Nauk, SSSR Ser. Geol. 1973, p 112. CA78, 13889 p (1973).

(159) Champlin, J. B. F., and Dunning, H. N., "Geochemical Investigation of Athabasca Bituminous Sands", Econ. Geol. 55 (4), p 747 (1960).

(160) Gleim, W. K. T., Gastsis, J. G., and Perry, C. J., "Occurrence of Molybdenum in Petroleum" in Reference 126.